MILITARY PYROTECHNICS

THE HISTORY AND DEVELOPMENT OF
MILITARY PYROTECHNICS

VOLUME 3
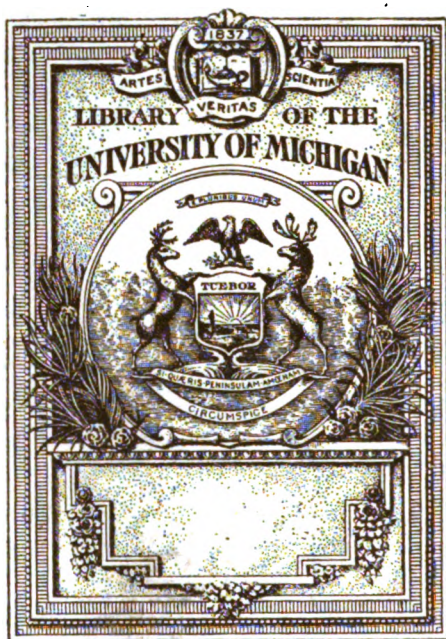
MILITARY PYROTECHNICS

A STUDY OF THE CHEMICALS USED IN THE MANUFACTURE OF MILITARY PYROTECHNICS

BY

HENRY B. FABER

DEAN OF THE PYROTECHNIC SCHOOLS
ORDNANCE DEPARTMENT
U. S. ARMY

IN THREE VOLUMES

VOLUME 3

PREFACE.

The purpose of this book is to describe from the standpoint of chemistry, the common materials used in the various branches of the manufacture of military pyrotechnics. Emphasis is laid on the occurrence, commercial methods of production, and physical properties of the chemicals, particularly those properties utilized in the manufacture of pyrotechnic articles.

In recommending specifications for the purchase of chemicals, we have attempted to limit the impurities occurring in such chemicals to a measure commensurate with the requirements for military pyrotechnic uses. These specifications have been set forth after consultation with the manufacturers, and the requirements for purity have been established with the idea of obtaining the maximum efficiency without placing an onus upon the manufacturer by demanding a quality of material beyond the actual needs. Consequently the requirements as set forth in the specifications are in all cases entirely within the range of good commercial practice.

In order that the manufacturer and the purchaser may come to some definite understanding in reference to the assay or analysis of the various chemicals, analytical methods have been recommended for determining the purity of the chemicals; developed with the idea of applying particularly to the requirements of this industry. Should the manufacturer of chemicals or pyrotechnic articles choose to install a laboratory for the purpose of analytical work, the services of a chemist would be required. In order to make the proper assays and analyses, a knowledge of elementary physics and general chemistry and particularly qualitative, quantitative analysis, both gravimetric and volumetric, is essential. It has been our aim in this work to simplify the methods of analysis so that a moderately well-equipped laboratory can handle all of the work required. In order thus to simplify the various methods, it became necessary to introduce certain

3

modifications in the methods of analysis practiced at the present time and also to develop new methods, representing original work.

The writer takes pleasure in acknowledging his indebtedness to his associates, Dr. Wm. B. Stoddard and Mr. M. A. Lindeman, and also to Dr. Ralph H. McKee, professor of engineering chemistry, Columbia University. It is also desired to express here appreciation of the courtesy shown by numerous manufacturers in furnishing information and making recommendations in reference to the quality of the materials.

HENRY B. FABER.

TABLE OF CONTENTS.

CHAPTER I.

SALTPETER, NITER, OR POTASSIUM NITRATE.

HISTORY.

The word salpeter is derived from two Latin words " sal," meaning salt, and " petra," a rock.

One of the earliest uses of potassium nitrate was as a component of the various pyrotechnic pieces used by the ancients, more particularly described in another part of this work. The first gunpowder made contained potassium nitrate, sulphur and charcoal, much as it does to-day.

Saltpeter was known to the Chinese at an early date. Its use in aiding combustion was well known, as mixtures of the salt with highly inflammable materials were used in striking fire with flint and steel. As is the case with most chemical substances used in early times, their desirable qualities were attributed more to mystic relations connected with their methods of manufacture than to the properties of the substances themselves.

The author of the works attributed to the Arabian Geber, who lived in the eighth century, was well acquainted with saltpeter or potassium nitrate, having used it in the making of nitric acid. Subsequent to Geber's time, potassium nitrate became well known to the alchemists.

In reviewing the history of the metals, it is to be noted that those occurring in the free state in nature were the first with which man became acquainted. On the other hand, those which occur in nature only in the form of compounds were isolated by man only after he had worked out processes for their reduction, tin and lead being examples of this class. Usually their isolation may be attributed to an accidental combination of conditions which would produce them, as no process of reasoning was available which would lead the experimenters to regulate conditions so that the production of the various metals might be expected.

7

As the metal potassium was one of the most difficult to reduce, it was not isolated in the metallic condition until produced by Davy in 1808 by electrolysis. In the same year it was also produced by Gay-Lussac and Thénard by heating caustic potash with metallic iron. Curadau, also, succeeded in obtaining the metal by substituting carbon for the iron.

OCCURRENCE IN NATURE.

Potassium nitrate, commonly known as niter, or saltpeter, is found in nature in very limited quantities. When so found it is in the form of white crusts, needlelike, orthorhombic crystals and silken tufts, occurring in limestone caverns or as incrustations upon the earth's surface, or on walls, rocks, etc. Exposure to the air does not change it. It is also formed in certain soils by the action of a ferment, especially after rains. Although found in small quantities in many of the so-called alkali lands of our western States, it is not utilized. Deposits in Ceylon and India are worked and refined niter produced.

METHOD OF MANUFACTURE.

Almost all of the saltpeter used in commerce is made from sodium nitrate and potassium chloride. In the process used, 80 per cent. pure potassium chloride, commonly known as muriate of potash, and commercial sodium nitrate—95 per cent. pure—are brought together with mother liquor from previous separations. The operation is performed in wrought-iron cylinders, 8 feet in diameter, 6½ feet high, provided with mechanical stirrers, steam coils and taps for open jets of steam; also with 6-inch pipes in the covers, through which the steam given off in the cylinders is passed through the double bottom of the mother-liquor tank. After boiling for one-half hour to complete the decomposition, a reaction takes place which is indicated in the following formula:

$$NaNO_3 + KCl = KNO_3 + NaCl.$$
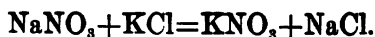
Owing to its relatively slight solubility in the hot concentrated solution, the NaCl or common table salt is almost entirely precipitated in crystalline form and retained on a filter, while the mother liquor at a temperature of 95° C. is

run off into the coolers. The separated salt is washed with liquor of decreasing strength, ultimately with pure water until the salt contains less than 1 per cent. of nitrate. The liquor in the cooler is kept agitated during the time of cooling, which is accomplished in 30 hours. This may be hastened by an outside-circulating water system. Potassium nitrate crystallizes out in these coolers and is subsequently recrystallized. This gives the double crystallized potassium nitrate of commerce, which is usually pure.

Saltpeter is also prepared from the potash salts obtained from the leaching of wood ashes, treating the burnt refuse from sugar beets, treating the liquors from wool-scouring, treating kelp ash, and by the decomposition of potash-bearing silicates.

All these methods are comparatively unimportant, although considerable experimental work has been done in this country during the war, one of the most extensive of which has been the cultivation of beds of kelp. The difficulty in preparing saltpeter for commercial purposes from these sources is due to the fact that potash is usually so contaminated with other salts as to render its purification by crystallization difficult.

The source of potash before the war was Stassfurt, Germany, where the minerals carnallite and kainite are found in vast beds in a soluble condition. These minerals are more-or-less-pure potassium chlorides which furnish the potash for the subsequent treatment with sodium nitrate to form saltpeter.

AVAILABILITY OF SUPPLY.

There is an unlimited quantity of soluble potassium-bearing minerals in the Stassfurt mines in Germany. There are extensive deposits of sodium nitrate, commonly known as Chile saltpeter in the celebrated nitrate fields of northern Chile. Small deposits of Chile saltpeter exist in Nevada, New Mexico, and California, and in the Republic of Colombia. The cultivation of kelp beds in the West, which has been carried on quite extensively during the war, may become a commercial source for potassium salts in the future. Potassium salts are also obtained in comparatively large quantities

from the potash lakes of western Nebraska and California, and as a volatile by-product in the cement industry, as well as from blast-furnace slag.

PHYSICAL PROPERTIES.

Color.—The salt consists of colorless, transparent, prismatic crystals or a crystalline white powder. The commercial product is slightly yellow, due probably to the presence of a small amount of iron impurity. The salt is odorless.

Solubility.—One hundred parts of cold water at 0° C. will dissolve $13\frac{3}{10}$ parts of saltpeter; 100 parts water will dissolve 247 parts at 100° C. It is practically insoluble in alcohol and ether.

Hygroscopicity.—It is a nonhygroscopic salt and does not change its physical character on exposure to the air.

Flame color.—Beautiful violet flame coloration is the characteristic of all potassium salts, of which saltpeter is an example.

Fusibility.—At between 336° and 353° C. saltpeter melts, and on continued heating it will decompose.

Taste.—It is salty and cooling, with a characteristic sharp saline taste.

Hardness.—It is a comparatively soft compound, having a hardness of 2 in a scale where diamond is 10 and talc is 1. The hardness is about the same as crystallized gypsum. It is easily ground.

Tenacity and opacity.—It is brittle in nature and translucent.

Specific gravity.—The specific gravity of the salt is 2.1 at 4°C.

CHEMICAL PROPERTIES.

GENERAL NATURE.

The molecular weight of saltpeter is 101.11; this is made up of potassium with an atomic weight of 39.10, nitrogen with an atomic weight of 14.01 and three atoms of oxygen with a total atomic weight of 48. The salt is neutral to litmus and does not change its chemical nature on exposure to the air. It is the potassium salt of nitric acid. It has no water of crystallization. It has the formula KNO_3.

REACTIONS.

The principal reactions of potassium nitrate are those which it shares in common with most other nitrates, its activity being due to the fact that it is a salt of nitric acid and when in a fused condition is a powerful oxidizer. Before the blowpipe on charcoal, it fuses easily, deflagrating violently like gunpowder and imparting the violet color characteristic of potassium salts to the flame. Nitric acid being a volatile compound, its salts are easily broken down when fused with other materials acid in their nature, which are nonvolatile. For example, tungstic anhydride (WO_3) or silica (SiO_2) when fused with potassium nitrate produces oxides of nitrogen and oxygen, empirically corresponding to N_2O_5. Borax and potassium bichromate will produce the same result. When treated with sulphuric acid, potassium sulphate and nitric acid are formed. The main characteristic of the salt, however, is its powerful oxidizing action when heated with a reducing material, such as charcoal, sulphur, sugar, and the like. The products formed by the action of the potassium nitrate on such reducing materials vary within wide limits, depending upon the proportions used and the conditions under which the experiments are conducted. When potassium nitrate is heated alone, oxygen is evolved and potassium nitrite (KNO_2) is formed.

FUNCTION IN PYROTECHNIC PIECES.

On account of the fact that saltpeter carries a large percentage of oxygen which is readily given up, it is peculiarly adapted to pyrotechnic compositions. In the presence of reducing agents, such as sulphur and charcoal, the liberation of this available oxygen takes place with such rapidity that an explosion follows, and it is this fact which is the underlying principle in its use for this work.

In most pyrotechnic work violent explosions are to be avoided, comparatively slow combustion being desired. This result is obtained by increasing the amount of inert materials or deterrents so that the combustion requires more time.

The proportions, which have been found over a period

of several centuries to be approximately balanced for securing the most efficient results in gunpowder, are:

	Per cent.
Potassium nitrate	75
Sulphur	10
Charcoal	15

By varying the percentages of these three ingredients, and by changing the sizes of the grains of the finished product, various forms of powder may be made, such as pebble powder, large-grain powder, fine-grain powder, sporting powder, mining powder, Spanish spherical powder, and cocoa powder. In order to see what takes place when such a mixture as the above is ignited, let us take the formula for a fine-grain powder, consisting of—

	Per cent.
Potassium nitrate	73.55
Potassium sulphate	.36
Potassium chloride	Trace.
Sulphur	10.02
Carbon	11.36
Hydrogen	.49
Oxygen	2.57
Ash	.17
Water	1.48

The composition of the solid and gaseous products from the explosion of this gunpowder was as follows:

Percentage composition by volume of the dry permanent gases.

	Per cent.
Carbon dioxide	50.62
Carbon monoxide	10.47
Nitrogen	33.20
Hydrogen sulphide	2.48
Methane	.19
Hydrogen	2.96
Oxygen	.08

Percentage composition by weight of the dry solid residue.

	Per cent.
Potassium carbonate	51.88
Potassium sulphate	22.71
Potassium monosulphide	18.16
Sulphur	6.90
Potassium thiocyanate	.18
Potassium nitrate	.17
Ammonium sesqui-carbonate	.05
Charcoal	None.

NOTE.—The sulphur in the above residue was determined as the higher sulphide of potassium.

One gram of dry powder when exploded liberates 738.3 gram-degree units of heat, and forms 263.1 c. c. of permanent gases at 0° C. and 760 mm. pressure. The total potential energy of gunpowder is estimated at about 340,000 kilogram-meters for 1 kilogram of powder, or a little under 500 foot-tons per pound. This calculation supposes the infinite expansion of the products of combustion. It is estimated, however, that the actual effective energy of gunpowder realized by modern guns varies from about $\frac{1}{10}$ to $\frac{1}{5}$ of the total theoretical amount. The temperature produced by the explosion of gunpowder is estimated at about 2,100° C. It is curious to note that potassium disulphide is one of the products of the combustion of black powder. This decomposition is assumed to take place in two stages; the first, an oxidation with the formation of potassium sulphate and carbonate, carbonic-acid gas, free nitrogen and perhaps carbonic oxide; and, secondly, a reduction in which free carbon and sulphur reduce the potassium sulphate and carbonate. The above table and data on the reactions and products of decomposition of gunpowder are taken from Thorpe's Dictionary of Applied Chemistry, volume 2, page 412.

USE IN PYROTECHNIC COMPOSITIONS.

Saltpeter is used in smoke-tracer compositions with sulphur and arsenic, to furnish the oxygen required for the combustion. It is used in the meal-power composition together with sulphur, black antimony, and dextrin; it is used in the aëroplane flare first-fire composition, together with barium nitrate, sulphur, and shellac. It is used in smoke-torch compositions together with pitch, borax, chalk, sand, and sulphur. Its function in all these mixtures is to furnish a source of oxygen in large quantities in a concentrated form.

ADVANTAGES.

Saltpeter has the advantage of being a cheap product in normal times, there being a large available source of supply of remarkably pure salt. Other advantages are its permanency in storage and on exposure to air, and relative safety in handling. It also has a large percentage of available oxygen on account of the fact that the atomic weight of

potassium is low as compared with other oxygen-liberating salts such as barium or strontium nitrates. It is non-poisonous and may be taken into the system without harmful effects, and is in fact used as a medicine.

ANALYSIS.

The following qualitative and quantitative methods for the analysis of saltpeter are based upon the assumption that the salt is the reasonably pure article known in commerce as "double refined."

QUALITATIVE TESTS.

Flame test.—This test shall be made in the ordinary manner by means of platinum wire moistened with concentrated hydrochloric acid, dipped in the powdered salt, and heated with a Bunsen burner. The test is made for the purpose of determining the purity of the salt in a very general way, in order to indicate the method of procedure.

Acidity.—Ten grams of the potassium nitrate shall be dissolved in 100 c. c. of distilled water. Delicate neutral blue litmus paper is inserted in the liquor and shall show no acid reaction after an immersion of 15 minutes.

Sulphates.—Five grams of the potassium nitrate shall be dissolved in distilled water and filtered. The filtrate is acidified with dilute hydrochloric acid, heated and a solution of barium chloride added. The formation of a white precipitate of barium sulphate indicates the presence of sulphates.

Soluble salts of iron.—Ammonia in excess shall be added to a fairly concentrated solution of the potassium nitrate, which has been brought to the boiling temperature. The presence of salts of iron is indicated by the formation of a precipitate of ferric hydroxide.

Salts of calcium.—If iron has been indicated as outlined in the foregoing paragraph, the precipitate is filtered off, a solution of ammonium chloride added, the solution heated to boiling, and treated with a small amount of ammonium oxalate. The formation of a white precipitate indicates the presence of soluble salts of calcium in the original material. After adding the ammonium oxalate, the solution shall be

allowed to stand not less than two hours in order that the precipitate shall have time to form.

Salts of magnesium.—If a precipitate of calcium oxalate is formed, as indicated above, the solution shall be filtered. Then a small amount of ammonium phosphate solution and a volume of concentrated ammonia equal to one-third the volume of the solution shall be added. The solution shall be allowed to stand in a cool place for at least 12 hours. The presence of salts of magnesium will be indicated by the formation of a white crystalline precipitate of ammonium magnesium phosphate.

Chlorides.—To a moderately concentrated filtered solution of potassium nitrate, a few drops of nitric acid shall be added, followed by a small amount of a solution of silver nitrate. The presence of soluble chlorides in the material will be indicated by the formation of a white precipitate of silver chloride. Traces will be shown as a turbidity in the solution.

The presence of any material amount of chlorides will indicate that salts of sodium may be found in the original material and serve as a guide for the later quantitative work.

The following results were obtained from the qualitative tests made upon a sample of commercial potassium nitrate used by one of the manufacturers of pyrotechnics:

Flame test_No material amount of sodium or calcium indicated.
Acidity_____Neutral.
Sulphates_____Absent.
Soluble salts of iron_____Absent.
Salts of calcium_____Trace.
Salts of magnesium_____Trace.
Chlorides_____Trace.

QUANTITATIVE TESTS.

Moisture.—A weighed sample of 5 grams shall be spread out on a 3-inch watch glass and dried in an air bath at 130° C. to constant weight. The loss in weight thus determined represents the amount of moisture present, and this loss divided by the weight of the sample taken will give the percentage of moisture.

Potassium nitrate.—One gram of potassium nitrate, which has been dried for the moisture determination, shall be mixed in a platinum crucible with approximately 5 grams of tungstic anhydride (WO_3), prepared by igniting tungstic acid in a platinum crucible with a blast lamp for one hour, and subsequently kept in a desiccator over sulphuric acid. The mixture shall then be heated gradually over a Bunsen burner, finally to quiet fusion. This generally requires not longer than ten minutes. The loss in weight represents the N_2O_5 content of the potassium nitrate, and this loss in weight multiplied by 1.872 will give the weight of the potassium nitrate in the sample tested, and this weight divided by the weight of the sample taken will give the percentage of the potassium-nitrate content.

Insoluble matter.—Five grams of the potassium nitrate shall be dissolved in 100 c. c. of boiling distilled water. The solution is then filtered through a Gooch crucible, which has been previously dried and weighed. After having been thoroughly washed with water, the crucible is dried at 100° C. for 30 minutes and weighed. The gain in weight represents the insoluble matter present. This gain divided by the weight taken will give the percentage of insoluble matter in the sample.

Chlorides.—To the filtrate from the insoluble matter above described, five drops of a 5 per cent. solution of potassium chromate shall be added and the chlorides then titrated with a one-fiftieth-normal solution of pure silver nitrate, the end point of the reaction being indicated by the appearance of the characteristic red color of silver chromate, which does not appear until all of the chlorides present have been precipitated by the silver nitrate.

Iron.—A solution of 5 grams of potassium nitrate in a little water shall be boiled for 15 minutes with 10 c. c. of concentrated nitric acid. After filtering and heating the solution to boiling, a slight excess of ammonia shall be added and the solution boiled for two minutes. It shall then be filtered through quantitative filter paper, thoroughly washed with hot water, ignited and weighed. The weight obtained represents the iron content of the material as Fe_2O_3, and this weight divided by the weight taken will give the percentage of the Fe_2O_3 content.

Calcium.—The filtrate from the iron determination outlined above shall be heated to boiling and an excess of ammonium-oxalate solution added. After standing not less than two hours the precipitate of calcium oxalate shall be filtered off, thoroughly washed with hot water, and titrated with a standard solution of postassium permanganate of approximately one-tenth-normal strength. An alternative method is to ignite before a blast lamp the paper and the precipitate of calcium oxalate and weigh as calcium oxide. If the latter method is adopted, quantitative filter paper shall be used for the filtration. The results shall be reported as calcium oxide.

Magnesium.—To the cold filtrate from the calcium determination as outlined above, 5 c. c. of a 10 per cent. solution of sodium or ammonium phosphate shall be added, and then one-third the total volume of the solution in concentrated ammonia; the solution shall then be allowed to stand for 12 hours in a cool place. Filter off the precipitated ammonium magnesium phosphate through a quantitative filter paper; wash with a cold dilute solution of ammonium chloride, ignite, and weigh as $Mg_2P_2O_7$. This weight multiplied by the factor 0.36207 will give the equivalent weight of MgO, and this weight divided by the weight of the sample taken will give the percentage of MgO.

Sodium.—The method recommended here for the determination of sodium oxide is an adaptation of Walter Craven Ball's method, found in the Chem. Soc. J. Trans. of 1909, page 2126 and the Chem. Soc. J. Trans. of 1910, page 1408. This method is based upon the fact that when a solution of potassium nitrite, bismuth nitrate, and caesium nitrate, acidified with dilute nitric acid, is added to solutions of sodium salts, even in the presence of large quantities of potassium salts, the sodium is precipitated as sodium-caesium-bismuth-nitrite having the formula $[Bi(NO_2)_3]_5$ $(CsNO_2)_9(NaNO_2)_6$, which carries 3.676 per cent. of sodium calculated as the metal, or 4.955 per cent. as Na_2O.

Calcium, magnesium, lithium, and ammonium do not interfere; chlorides should not be present in greater concentration than one-fifth normal. If phosphates are present in more than a trace, they may be removed by heating the solution to 100° C. and treating with a solution of pure potassium nitrite, to which bismuth nitrate has been added.

Iodides, citrates, and salts of hydroxy, acids, and most of the heavy metals, particularly silver, interfere with the results. Sulphates, nitrates, nitrites, acetates and formates, however, do not interfere. The determination of very small amounts of sodium may be made with great accuracy, even in the presence of large quantities of potassium salts which are soluble under the conditions of precipitation.

REAGENT FOR SODIUM DETERMINATION.

The reagent which is used is prepared as follows:

Thirty grams of pure potassium nitrite, which should be free from sodium, are dissolved in a little water. The potassium nitrite should contain little free alkali; the presence of small amounts of sodium in the potassium nitrite causes a waste of the caesium nitrate which is later added, and for this reason should be avoided. To this are added 3 grams of bismuth nitrate dissolved in a little dilute nitric acid. The solution of bismuth nitrate is prepared by dissolving 40 grams of the crystallized salt made up to 50 c. c. with approximately twice normal HNO_3; 3¾ c. c. of this solution will contain 3 grams of bismuth nitrate. Should the resulting solution be turbid, which may occur if the nitrite contains free alkali, dilute nitric acid must be added until it is clear, then 16 c. c. of a 10 per cent. solution of caesium nitrate are added, and the volume made up to 100 c. c. with water; or if turbid, with water and a little nitric acid. The reagent is allowed to stand for two days, when the sodium present, as an impurity, will have been precipitated. This precipitate should then be filtered off. It is also desirable to keep the reagent under coal gas, as the action of the air causes a scum to separate out, which must be removed before the reagent can be used. Variations in the preparation of the reagent from the above method and proportions should be avoided, as it will interfere with the accuracy of the determination. 1 c. c. of this reagent will precipitate from 0.5 to 0.7 mgrms. of sodium.

The white scum which may appear on the surface of the reagent is probably due to two different reactions:

$$2Bi(NO_2)_3 + O_2 + 2H_2O = 2BiONO_3 + 4HNO_2.$$
$$Bi(NO_2)_3 = BiONO_3 + 2NO.$$
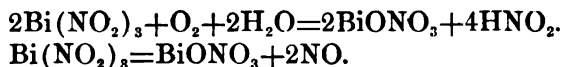
The reagent may be kept for several weeks if it is protected from the air in the manner indicated.

The proportions of potassium nitrite may be lowered to 25 or 20 grams per 100 c. c., but such a reagent does not keep well, and appears to be less trustworthy. The amount of bismuth nitrate may be increased to 6 grams or more, but again this reagent is much less stable, though it causes a more rapid precipitation; less than ·3 grams of bismuth nitrate per 100 c. c. must not be used. An addition of caesium nitrate beyond 1.6 to 1.8 grams per 100 c. c. of reagent causes the weight of precipitate to be too large. More than 2 grams of caesium nitrate per 100 c. c. produces a precipitate of hexagonal plates of caesium bismuth nitrite, and it is possible that an admixture of this compound is the cause of the too high weight of precipitate obtained when the reagent contains more than 1.6 to 1.8 grams of caesium nitrate per 100 c. c. When these precipitates are examined with a microscope they appear to be free from hexagonal crystals of caesium bismuth nitrite, and they appear to be homogeneous. A possible explanation is that in the sodium, caesium, bismuth nitrite, the atomic ratio of caesium to sodium varies from 3:2 to 2:1, as indicated in the formulas $9CsNO_2$, $6NaNO_2$, $5Bi(NO_2)_3$, and $2CsNO_2$, $NaNO_2$, $Bi(NO_2)_3$. Lower concentration of caesium when the concentration of potassium nitrite is also lower will form a precipitate; for instance, if the reagent contains 30 grams of potassium nitrite and 2 grams of caesium nitrate per 100 c. c., no hexagonal plates will be deposited; but when 15 grams of potassium nitrite and 2 grams of caesium nitrate are added, more than 1 gram of caesium bismuth nitrite is obtained.

If a reagent is desired to give a more rapid precipitation, this might be effected by increasing the concentration of the caesium and determining by research the factor to convert the weight of the precipitate into the weight of sodium. The quantitative determination of any of the three metals, sodium, caesium or bismuth, may be made by the presence of a large excess of the other two. If the reagent is prepared in the manner outlined, the Na_2O content is such that when the weight of the precipitate is multiplied by 0.0495 the result will give the weight of the Na_2O present.

OPERATION.

One gram of potassium nitrate shall be dissolved in 5 c. c. or less of water and placed in a 30 c. c. Erlenmeyer flask, and 1 c. c. of dilute nitric acid, twice normal, is added, and by means of a pipette, 10 c. c. of the reagent are added. The mixture is well stirred and coal gas passed through the flask

FIG. 1.

for one minute. Several of the Erlenmeyer flasks may be placed in series when a number of determinations are made. This is indicated in figure No. 1.

After passing through coal gas for one minute one end of the series is closed by a glass plug and the other by a Bunsen

FIG. 2.

valve, which is used in order to permit the escape of ni-trous fumes which are generated in small amounts.
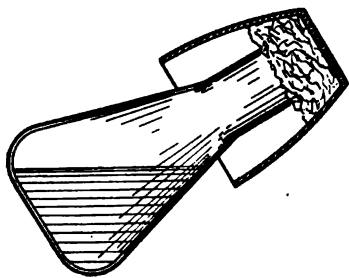
The sodium-cæsium-bis-muth nitrite will begin to separate within a few minutes, and will collect in the bottom of the flask, as a yellow crystalline precipitate. After 36 to 48 hours no scum should appear on the surface of the liquid. The stopper is removed and the flask is rotated and tilted to an angle insufficient for the liquid to run out, and the neck of the flask placed against the asbestos pad, in a Gooch crucible, as indicated in figure No. 2, which has previously been prepared by mixing the asbestos with twice-normal nitric-acid solution and packing. This padding should fill the crucible one-third full. (The crucible is prepared by adding 10 c. c. of 50 per cent. acetone solution, followed by 15 c. c. of pure acetone in three portions, the acetone being removed by suction. The

crucible shall then be dried in an air bath at 100° C. for 30 minutes.) The crucible is tilted at such an angle as to avoid any possible loss of the asbestos pad, and the crucible rapidly righted, as indicated in figure No. 3, when the flask will be found in an inverted position, the neck resting tightly on the asbestos pad. In this position the flask and crucible are ro-tated with a slight vertical motion, which will wash all of the precipitate from the bottom of the flask, and the flask is then slowly raised, permitting the solution to enter the cru-cible, and the neck carefully withdrawn with a slight rotary motion, to wash off any adhering particles of the precipitate or asbestos.

The thickness of the asbestos pad is sufficient to prevent any solution from going through it until the crucible has been placed in a suction funnel. Suction is applied rapidly until three-fourths of the solution is passed through the crucible, when suction is re-leased. A small amount of the filtered solution is returned to the flask and a "policeman" used to remove any part of the precipitate that may have been attached to the sides, and transferred to the crucible, and suction again applied. The solution is rapidly filtered and the sides of the cru-cible are washed with 5 c. c. of a 50 per cent. acetone solution by means of a very fine stream from a minature graduated wash bottle. Suction is applied until

FIG. 3.

the solution has been passed through, and then 15 c. c. of pure acetone are added in three portions, each portion being passed through the filter by suction and the suction stopped before the next portion is added. The filtering op-eration should be done as rapidly as possible and a very small filter flask used, the object being to avoid exposure of the precipitate, in the presence of the reagent, to access of air, as much as possible. Should a small amount of scum on the sides of the flask or crucible appear during the sec-ond filtration, it may be disregarded, as it has no perceptible effect on the estimation. The filtrate should be perfectly clear before the acetone is used. The crucible is then dried in an air bath at 100° C. for 30 minutes and weighed. The
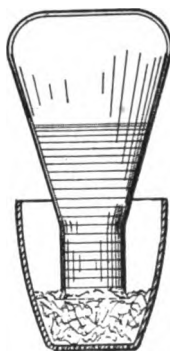
weight of precipitate multiplied by 0.03676, will give the weight of the sodium, calculated as the metal in the original salt.

As the complex precipitate is a nitrite it is susceptible to titration by potassium permanganate, according to the following procedure: After having been dried as described, the precipitate together with the asbestos from the crucible is transferred to a beaker, 150 c. c. of water are added, followed by a known volume of a standard solution of approximately one-tenth-normal potassium permanganate in excess of the amount required for the oxidation; 40 c. c. of sulphuric acid (1:1) are added and the solution heated to 70° C. The excess of potassium permanganate is then titrated by means of a standard solution of sodium oxalate of approximately one-tenth-normal strength. The available oxygen of the permanganate consumed in the oxidation of the precipitate under the acid conditions prevailing, multiplied by 7.820, will equal the weight of the bismuth cæsium sodium nitrite precipitate, as 30 atoms of oxygen are required for each molecule of bismuth-cæsium-sodium nitrite in order to convert the nitrites to the nitric state of oxidation. Extended tests have established the availability of this volumetric method.

The filtrates from these determinations should be saved in order that the cæsium may be later recovered. The cæsium is recovered by the addition of silver nitrate in slight excess, which precipitates a very insoluble silver-cæsium-bismuth nitrite. This on heating and subsequent extraction with water yields a pure cæsium salt.

From the factor given (0.03676) it will appear that 1 mgm. of sodium will produce over 27 mgms. of precipitate, and consequently the amounts of various materials to be taken for analysis must be gauged according to their probable sodium content. From 3 to 8 mgms. of sodium content will be found to be a very convenient amount for this method. The crystals are a golden-yellow color, clear, relatively coarse, and easy to filter, and on microscopic examination show no evidence of the presence of impurities. They are octahedral in form.

The following quantitative results were obtained on the analysis of a doube refined commercial saltpeter:

No. 1. *Moisture:*

	Grams.
Weight taken_____	3.0950
Weight after drying_____	3.0859
Loss in weight_____	.0001

This is equivalent to 0.3 per cent.

No. 2. *Potassium nitrate:*

	Grams.
Weight dried potassium nitrate taken_____	1.00
Loss in weight_____	.5318

This loss in weight multiplied by 1.872 gives the weight of the potassium nitrate in the dried sample. This is found to be 0.9955 gram of potassium nitrate, which is equivalent to 99.55 per cent.

No. 3. *Insoluble matter:*

	Grams.
Weight taken ____ _____ ___ . . _____	5.00
Weight of insoluble matter_____	.002

This is equivalent to 0.04 per cent.

No. 4. *Chlorides.*—The weight of potassium nitrate taken was 5 grams. The titration with silver nitrate required 1½ c. c. The chlorine value of the silver-nitrate solution was 0.00179 gram per cubic centimeter. The chlorine value multiplied by the number of cubic centimeters required will give the weight of chlorine found, which is equal to 0.002685 gram, which divided by the weight taken is equal to 0.054 per cent.

No. 5. Fe_2O_3.—As the test for iron salts was negative and also the total percentage of insoluble matter was only 0.04 per cent., a trace only of iron compounds may be reported in the sample analyzed.

No. 6. CaO.—A test showing the practical absence of calcium salts, a trace only is reported.

No. 7. MgO.—A trace only of this substance was found.

No. 8. Na_2O.—No trace of sodium compounds could be found in an appreciable amount.

VOLUMETRIC DETERMINATION OF SODIUM.

As the precipitate produced in this sodium determination is a nitrite, attempts were made to determine its amount by

titration with a solution of potassium permanganate. A solution of this salt was carefully standardized by means of a standard solution of sodium oxalate, and the oxygen equivalent under acid conditions of each cubic centimeter of the potassium-permanganate solution was found to be 0.007176 gram.

The asbestos containing the precipitate was removed from the Gooch crucible and placed in a beaker containing 10 c. c. of the standard permanganate solution diluted with about 200 c. c. of water. Fifty cubic centimeters of sulphuric acid (1:2) were then added and the solution heated to from 70° to 80° C. The asbestos was thoroughly stirred through the solution, and the excess of permanganate was titrated by the sodium-oxalate solution before mentioned. In the two original tests, amounts of precipitate weighing 0.0616 gram and 0.0653 gram were used. In the first case 10 c. c. of the permanganate solution and in the second case 12 c. c. were used; 0.8 c. c. and 2.7 c. c. of the oxalate solution, respectively, were required for the excess of permanganate. The amount of available oxygen consumed by the two precipitates was 0.007 gram and 0.007159 gram, respectively. Each molecule of the precipitate, $5Bi(NO_2)_3 9CsNO_2 6NaNO_2$, requires 30 atoms of oxygen in order to convert the nitrites to the nitric state of oxidation. Consequently, the weight of oxygen consumed multiplied by the factor 7.82 should give the weight of the precipitate. Using this factor, with the weight of oxygen consumed in the two instances given, we made for the weight of precipitate used 0.0548 gram and 0.056 gram, respectively, where the precipitates themselves weighed 0.0616 gram and 0.0653 gram; or, in other words, the volumetric results were too low.

These precipitates stood in the air for a period of six days before the titration, during which time they were subject to oxidation.

In order to test the volumetric method on freshly prepared precipitates, a series of four determinations was run, in which the precipitates were titrated immediately after weighing them. The results were tabulated as follows:

Comparison of gravimetric with volumetric method.

No.	Gravimetric.		Volumetric.		Calculated weight of Ppt.
	Weight of Ppt. in grams.	c. c. KMnO₄ used.	c. c. Na₂C₂O₄ used.	Weight O. consumed in grams.	
1...............	0. 0739	15	2. 8	0. 00936	0. 0732
2...............	. 0671	15	3. 7	. 00872	. 0682
3...............	. 0662	15	4. 2	. 00836	. 0654
4...............	Not weighed.	15	3. 5	. 00886	. 0693

From these results it is evident that the volumetric method is applicable to this determination, and its use will result in a great saving of time.

SPECIFICATIONS.

In connection with the investigations made upon potassium nitrate, the following specifications should be adopted for the potassium nitrate to be used in military pyrotechnics:

No. 1. The material should be white or at least show only a slight yellowish tinge.

No. 2. The material shall be odorless.

No. 3. When compounded, the material shall be ground so that all will pass through an 80-mesh and 60 per cent. will pass through a 100-mesh sieve.

No. 4. The material shall contain not less than 99 per cent. of potassium nitrate.

No. 5. The material shall contain not more than 0.2 per cent. of moisture when compounded.

No. 6. The dry material shall contain not more than 0.5 per cent. of calcium or magnesium salts, or of both together, calculated as oxides.

No. 7. The dry material shall contain not more than 0.5 per cent. of iron compounds, calculated as Fe_2O_3.

No. 8. The material shall contain not more than 0.25 per cent. of sodium salts, calculated as Na_2O.

No. 9. The material shall contain no free acid.

DISCUSSION OF THE SPECIFICATIONS FOR SALTPETER.

Concerning points Nos. 1, 2, 3, the specifications regarding the color, odor, and fineness of materials which are acceptable for use, are statements of the properties of material now in use which are known to give satisfaction. The physical properties of the potassium nitrate found in commercial practice are within the requirements under the specifications Nos. 1, 2, and 3.

Potassium nitrate containing more than 0.2 per cent. of moisture when compounded is difficult to handle, owing to the fact that the ground crystals tend to form lumps and become solid masses, preventing uniformity in mixing the compositions in which it is used.

The presence of calcium and magnesium salts in the potassium nitrate in excess of the percentages specified, will cause deliquescence, and in the case of calcium, flame deterioration.

The presence of more than 0.5 per cent. of iron impurities as Fe_2O_3 has a deteriorating effect upon the color of the flame produced by strontium nitrate, and for that reason this limit should be set for the iron content of potassium nitrate. The presence of 0.5 per cent. of Fe_2O_3 in potassium nitrate will probably not affect its use in propelling charges, but as it may be used for light-producing compositions it is likewise well to set 0.5 per cent. as the limit. Samples of the commercial article examined were well within the above limit.

The percentage of sodium, calculated as Na_2O in potassium nitrate, should never be permitted to exceed the limit set, for the following reasons:

First. The presence of Na_2O in excess of 0.2 per cent. will cause the rapid absorption of a considerable amount of moisture.

Second. When the potassium nitrate is used in the flame-coloring compositions, a percentage of sodium in excess of the limit set will change the color of the flame desired.

Any free acid present will cause a rapid decomposition in the mixtures in which the potassium nitrate is used.

26

CHAPTER II.

STRONTIUM NITRATE.

HISTORY.

Strontianite, from which strontium nitrate was first made, takes its name from Strontian, in Argyllshire, where it appears to have been known as far back as 1764, but it was not recognized as a distinct mineral until later, when the examination of it led to the discovery of the element strontium.

OCCURRENCE IN NATURE.

Strontium nitrate does not occur as such in nature. The most important source of strontium salts is the mineral celestite, which is the sulphate of strontium. This occurs as a white translucent mineral, often with a faint bluish tinge. It occurs in tabular or prismatic orthorhombic crystals, fibrous and cleavable masses, and rarely granular. It is notably heavy and has a general resemblance to barite, which is the sulphate of barium. The mineral is found frequently in cavities, in limestone, marl, or sandstone, or in beds of gypsum, or in volcanic regions, with sulphur, gypsum, etc. The most important source of this mineral at the present time is England. The island of Sicily contains celebrated deposits of this mineral. In the United States deposits occur on Strontian and North Bass Island, Lake Erie; at Bells Mills, Pa.; in Chaumont Bay, Lockport; and other places in western New York. It is also found in Kansas, Texas, West Virginia, Tennessee, and Southern California; also at Kingston, Canada. The mineral has a hardness of 3 to 3.5 and a specific gravity of 3.95 to 3.97.

METHOD OF MANUFACTURE.

Strontium nitrate is prepared at the present time almost entirely from celestite, as above indicated. Two processes are utilized for this purpose:

27

First. The celestite, after being ground, is mixed with coke or coal and roasted until the sulphate of strontium is reduced and converted into strontium sulphide; this being soluble in water is leached and strontium carbonate precipitated with soda ash. After being thoroughly washed, the strontium carbonate is dissolved in dilute nitric acid, yielding a solution of strontium nitrate from which the salt crystallizes on evaporation. A second crystallization of the material is not found necessary if the process has been properly conducted.

Second. Finely ground celestite is boiled with a solution of sodium carbonate of appropriate strength, thus transforming the strontium sulphate into strontium carbonate. The strontium carbonate, after being well washed, is dissolved in dilute nitric acid, and the resulting solution of strontium nitrate filtered off and the salt obtained by crystallization. Either of these processes will yield a product which is white or slightly yellowish in color and which has been found to be approximately 99.5 per cent. pure.

AVAILABILITY OF SUPPLY.

In American practice at the present time strontianite is not used, probably because it can not be obtained in large quantities in a pure condition. The American deposits of celestite appear to be scattered, and, according to the descriptions, the mineral is largely contaminated with foreign matter. The California deposits have been worked to only a very limited extent, and while the quality of the product is fairly satisfactory, the deposits are located a long distance from a railroad, and a steady production would be extremely difficult to attain; consequently, the manufacturers of strontium salts in this country import their celestite from England, the low water freight and the continuity of the deposits there permit the delivery of the material at the Atlantic coast ports at about one-half the price under normal conditions of the American product.

There is an almost unlimited source of supply of nitric acid, which is used in the preparation of strontium nitrate; one principal source being the condensation of the fumes formed in the nitration of cotton, which yield nitric acid as a by-product.

PHYSICAL PROPERTIES.

Color.—The commercial product is a yellowish-white crystalline powder; the crystals belong to the regular system, forming generally in octahedra, modified by faces of the cube.

Solubility and water of crystallization.—100 parts of water at 0° C. will dissolve 39.5 parts of strontium nitrate; 100 parts of water at 100° C. will dissolve 101.1 parts.

Strontium nitrate is practically insoluble in absolute alcohol, 100 parts dissolving 0.024 part at ordinary temperatures. It is slightly soluble in rectified spirits, 100 parts dissolving 0.5 parts. It is almost insoluble in strong nitric acid. It is almost entirely insoluble in amyl alcohol.

When strontium nitrate is crystallized from hot concentrated solutions, the anhydrous salt separates out in transparent crystals; on cooling a dilute solution of strontium nitrate, the salt, carrying 4 molecules of water of crystallization, separates out in large triclinic crystals, which rapidly effloresce in the air. When the crystallization is done below 31° C. the anhydrous strontium nitrate is formed; when the crystallization takes place above 31° C. the salt crystallizes out with 4 molecules of water of crystallization.

Hygroscopicity.—This salt is generally considered the most hygroscopic of the available nitrates for use in pyrotechnic pieces. It has been found, however, on an examination of the ordinary commercial strontium nitrate, that when it is dried at 110° C. it loses but 0.25 per cent. of moisture. When, however, this dried salt is heated to 260° C. and then exposed to the air for a period of one week, the salt reabsorbs only the moisture which it lost when heated between 110 and 260° C.

Flame color.—A beautiful crimson flame coloration is characteristic of all strontium salts of which strontium nitrate is an example. The clear crimson red of the flame coloration by pure strontium salts is seriously impaired by the presence of very small amounts of the salts of certain other metals, such as sodium and calcium. The presence of traces of sodium salts is sufficient to give the characteristic yellow flame. Calcium salts also are discernible if in very small amounts by the flame coloration, consequently the pres-

ence of either or both of these metals has a very serious effect on the shade of the colored flame produced by strontium salts. Commercial samples of strontium nitrate examined produce a flame greatly inferior to that of pure strontium nitrate, even though the analysis shows the presence of no weighable amount of sodium compounds and only 0.044 per cent. of calcium salts, calculated as the oxide.

The sodium and calcium impurities found in the commercial strontium nitrate seem to produce their flame effect before the strontium salts show the density of red which they finally produce. In the burning of pyrotechnic pieces containing strontium nitrate, the light produced in the initial effect will therefore be the intensified result of the sodium and calcium compounds present, particularly as the functioning of the pieces allows no time for the strontium compounds to purify themselves by the volatilization of the sodium and calcium salts. Consequently any study of flame colorations as produced by commercial salts must be so regulated that the observations are made immediately after the introduction of the material into the flame and without waiting for the volatilization of the sodium and calcium compounds which are the first observed. Flame tests must be devised in which the supply of the flame-coloring material shall be fed into the heated zone continually, and all the conditions must be uniform in order to attain anything like comparable results. There is no doubt but that the burning of the briquettes used for producing colored-flame effects, used in the various pyrotechnic pieces will give the initial effect of the sodium and calcium content in an intensified form, as the burning mass has no opportunity to rid itself of these impurities by long-continued combustion.

Fusibility.—It is not a volatile compound, but at high temperatures it decomposes.

Taste.—It possesses a cool taste, somewhat salty and bitter.

Hardness.—The crystals are soft and easily ground.

Tenacity and opacity.—The crystals are friable and transparent.

Specific gravity.—The specific gravity according to Schröder is 2.96 at 4° C.

CHEMICAL PROPERTIES.

GENERAL NATURE.

The molecular weight of anhydrous strontium nitrate is 211.65; this is made up of strontium with an atomic weight of 87.63, 2 atoms of nitrogen with a total atomic weight of 28.02, and 6 atoms of oxygen with a total atomic weight of 96. The salt is neutral to litmus and does not change its chemical nature on exposure to the air. It is the strontium salt of nitric acid and has the formula $Sr(NO_3)_2$.

REACTIONS.

Like potassium nitrate, the principal reactions of strontium nitrate are those of salts of nitric acid. When thrown upon red-hot charcoal it deflagrates, burning with a red flame. When heated with tungstic anhydride (WO_3) or silica (SiO_2), oxygen and the oxides of nitrogen are formed. Borax and potassium bichromate will produce the same result. When strontium nitrate is treated with sulphuric acid, a sulphate is formed and nitric acid liberated. The products formed by the action of strontium nitrate on such reducing materials as charcoal and sulphur under the influence of heat are similar to those formed when saltpeter is so treated.

FUNCTION IN PYROTECHNIC PIECES.

Strontium nitrate has two functions in pyrotechnic compositions:

First. The flame color which it produces and which has already been discussed.

Second. The fact that it is a nitrate and as such plays the part of a powerful oxidizer when heated with any reducing material such as shellac, charcoal, and the like.

PYROTECHNIC COMPOSITIONS.

The common uses for strontium nitrate are in the following compositions:

> Red position lights.
> Red signal lights.
> Red stars.
> Red-tinge wing-tip flare.

Typical compositions used in the above are as follows:

	Per cent.
Potassium chlorate	37½
Strontium nitrate	50
Shellac	12½

In this composition the oxygen necessary for the combustion of the shellac is produced both by potassium chlorate and the strontium nitrate. The function of the shellac is twofold in its nature: It acts, first, as a binding material for the composition, whether it be briquetted or pounded or pressed into a case, and, second, it is the fuel which consumes the oxygen from the salts. The combustion of the shellac furnishes the heat for the flame coloration. Another manner in which the salt acts is as follows:

Red-tinge wing-tip flare:

	Per cent.
Strontium nitrate	66⅔
Sulphur	16⅔
Aluminum (powdered)	16⅔
Shellac binder.	

In this composition the oxygen from the strontium nitrate is consumed by sulphur and aluminum, the aluminum furnishing the high temperature desired and the sulphur retarding the spread of combustion, so that the flame may last the desired length of time. As in the other compositions strontium gives also the red color to the flame.

ADVANTAGES.

The salts of strontium are the only available salts for the production of a red color in flame compositions. Lithium and calcium compounds give red flames; but lithium salts are comparatively rare and not available in commercial quantities, and calcium compounds lack the depth of shade required for signaling purposes, the flames therefrom being more of an orange red than a scarlet red.

The use of strontium nitrate in pyrotechnic compositions is peculiar in that it furnishes not only the oxygen necessary, but also imparts the characteristic red color desired. Its use for this purpose was adopted shortly after its discovery in 1764.

ANALYSIS.

The following qualitative and quantitative methods for the analysis of strontium nitrate are based upon the assûmption that the salt is the reasonably pure product found in commerce.

QUALITATIVE TESTS.

Flame test.—This test shall be made in the ordinary manner by means of platinum wire moistened with concentrated hydrochloric acid, and dipped in the powdered salt and heated with a Bunsen burner. This test is made for the purpose of determining the purity of the salt in a very general way, in order to indicate the method of procedure.

Acidity.—Ten grams of strontium nitrate shall be dissolved in 100 c. c. of previously boiled distilled water. Delicate neutral litmus paper is inserted in the liquor and shall show no acid reaction after an immersion of 15 minutes.

Sulphates.—Five grams of the strontium nitrate shall be dissolved in distilled water and filtered. The filtrate is acidified with dilute hydrochloric acid, heated, and a solution of barium chloride added. The formation of a white precipitate of barium sulphate indicates the presence of sulphates.

Soluble salts of iron.—Ammonia in excess shall be added to a fairly concentrated solution of the strontium nitrate, which has been brought up to the boiling temperature. The presence of salts of iron is indicated by the formation of a precipitate of ferric hydroxide.

Salts of calcium.—This examination shall be made qualitatively as described under the quantitative analysis of the calcium in strontium nitrate.

Salts of magnesium.—A solution of strontium nitrate shall be treated with an ammoniacal solution of ammonium chloride and ammonium carbonate, whereby strontium carbonate is precipitated. This is filtered off and washed and the filtrate treated with a small amount of ammonium-phosphate solution and a volume of concentrated ammonia, equal to one-third the volume of the solution, shall then be added. The solution shall be allowed to stand in a cool place for at least 12 hours. The presence of salts of magnesium will be

indicated by the formation of a white crystalline precipitate of ammonium-magnesium phosphate.

Chlorides.—To a moderately concentrated filtered solution of strontium nitrate, a few drops of nitric acid shall be added, followed by a small amount of a solution of silver nitrate. The presence of soluble chlorides in the material will be indicated by the formation of a white precipitate of silver chloride. Traces will be shown as a turbidity in the solution.

The presence of any material amount of chlorides will indicate that salts of sodium may be found in the original material and serve as a guide for the later quantitative work.

The following results show the qualitative tests made upon a commercial sample of strontium nitrate:

Flame test: No flame discoloration was noted.
Acidity: None.
Sulphates: Absent.
Chlorides: Trace.
Soluble salts of iron: Trace.
Salts of calcium: Trace.
Salts of magnesium: Trace.

QUANTITATIVE TESTS.

Moisture.—A weighed sample of 5 grams shall be spread out on a 3-inch watch glass and dried in an air bath at 130° C. to constant weight. The loss in weight thus determined represents the amount of moisture present.

Acidity.—This might properly be called alkalinity when applied to strontium nitrate, as the presence of strontium carbonate in the insoluble portion will give an alkaline reaction. To determine this 5 grams of material shall be dissolved in warm water and titrated with a one-fiftieth normal solution of sulphuric acid, using methyl orange as an indicator.

Strontium nitrate.—One gram of strontium nitrate which has been dried for the moisture determination is mixed in a platinum crucible with approximately 5 grams of tungstic anhydride prepared by igniting tungstic acid in a platinum crucible with a blast lamp for one hour and subsequently

kept in a desiccator over sulphuric acid. The mixture shall then be gradually heated over a Bunsen burner for about 10 to 15 minutes. The tungstate of strontium being infusible, the mass will not melt down. The ignition, however, is very quiet, which is insured by a careful heating of the salt before using until all decrepitation has ceased. The loss in weight is equivalent to the N_2O_5 content of the strontium nitrate, and this loss in weight multiplied by 1.959 will give the weight of the strontium nitrate in the sample tested.

Insoluble matter.—Five grams of the strontium nitrate shall be dissolved in 100 c. c. of boiling distilled water. The solution is then filtered through a Gooch crucible which has been previously dried and weighed. After having been thoroughly washed the filter flask is changed and the residue washed three times with pure acetone. The crucible is then dried at 100° C. for 30 minutes and weighed. The gain in weight represents the insoluble matter present.

Chlorides.—To the filtrate from the insoluble matter above described, five drops of a 5 per cent. solution of potassium chromate shall be added and the chlorides then titrated with a one-fiftieth normal solution of pure silver nitrate, the end point of the reaction being indicated by the characteristic red color of the silver chromate, which does not appear until all of the chlorides present have been precipitated by the silver nitrate.

Iron.—A solution of 5 grams of strontium nitrate in a little water shall be boiled for 15 minutes with 10 c. c. of concentrated nitric acid. After filtering and heating the solution to boiling, a slight excess of ammonia is added and the solution boiled for two minutes. It is then filtered through quantitative filter paper, the precipitate thoroughly washed with hot water, ignited and weighed. The weight obtained represents the iron content of the material as Fe_2O_3.

Calcium.—The separation of calcium from strontium nitrate depends upon the solubility of calcium nitrate in amyl alcohol, and the relative insolubility of strontium nitrate in the same solvent. To this end 1 gram of the salt shall be dissolved in the least possible amount of hot water in a 150 c. c. beaker, and 30 c. c. of amyl alcohol added, and boiled

until the boiling point of amyl alcohol is reached, which is between 128° and 130° C. When this temperature is reached, the volume of the solution will be found to have diminished between one-third and one-half. The water present will have been evaporated and the calcium nitrate will have gone into solution in the amyl alcohol to the exclusion of the strontium nitrate, which is left as a residue. This is filtered off through a perfectly dry Gooch crucible, which has been previously prepared by washing with water-free amyl alcohol and drying. The beaker shall be rinsed three times with amyl alcohol, passing the alcohol wash through the crucible. The filtering operation should be done in the cold to reduce the solubility of the strontium nitrate. The filtrate shall then be evaporated to dryness without baking and taken up with water and boiled. The calcium shall be precipitated by ammonium oxalate from an ammoniacal solution to which ammonium chloride has been added. A great excess of ammonium oxalate is required in order to complete the precipitation. On standing over-night the precipitate shall be filtered off and washed with a dilute solution of ammonium oxalate. The precipitate and filter shall then be ignited and weighed as calcium oxide. When small quantities of calcium are present this ignition may be completed in 15 minutes in a platinum crucible.

As strontium nitrate is somewhat soluble in amyl alcohol, the results must be corrected. It has been found by a long series of experiments that this correction is equivalent to 0.0004 gram of strontium oxide for each 10 c. c. of amyl alcohol used in the original separation. The cold alcohol subsequently used to wash the precipitated strontium nitrate does not carry any of the salt into solution, so it is unnecessary to make any correction for its use.

Magnesium.—Five grams of material shall be dissolved in hot water and an excess of ammonium chloride and ammonium carbonate shall be added and the solution boiled and filtered. To the filtrate a small amount of a solution of sodium or ammonium phosphate shall be added, followed by one-third of the total volume of solution in concentrated ammonia. The solution shall then be allowed to stand for 12 hours in a cool place. The precipitated ammonium-magnesium phosphate shall be filtered off, washed with a cold

dilute solution of ammonium chloride, ignited, and weighed as $Mg_2P_2O_7$.

Sodium.—One gram of strontium nitrate shall be dissolved in 5 c. c. or less of water, placed in the usual 30 c. c. Erlenmeyer flask and the sodium precipitated and determined as indicated in the chapted on potassium nitrate.

The following is an example of the analysis of a commercial sample of strontium nitrate:

1. *Moisture:*

	Grams.
Weight taken_____	4.45
Weight after drying_____	4.4387
Loss in weight_____	.0113

This is equivalent to 0.25 per cent.

2. *Strontium nitrate:*

	Grams.
Weight of platinum crucible_____	20. 3983
Weight of the crucible plus WO_3_____	24. 4537
Weight of crucible plus WO_3 plus strontium nitrate_	25. 4570
Weight of strontium nitrate taken_____	1. 0083
Weight after fusion_____	24. 9480
Loss in weight_____	.509

This loss in weight multiplied by the factor 1.959 gives the weight of strontium nitrate in the dried sample. This is found to be 0.9971 gram of strontium nitrate, which is equivalent to 99.38 per cent.

3. *Insoluble matter:*

	Grams.
Weight taken_____	10
Weight Gooch crucible plus insoluble matter_____	16. 0438
Weight Gooch crucible_____	16. 0245
Weight insoluble matter_____	.0193

This is equivalent to 0.193 per cent.

4. *Chlorides.*—A trace only of compounds of this element was found.

5. *Fe_2O_3.*—Both the soluble and insoluble portions showed only traces of iron compounds.

6. *CaO.*—Weight of platinum crucible plus CaO plus strontium oxide from the ignition of the oxalates, 19.3920 grams.

Weight of platinum crucible, 19.3910 grams.

Weight of CaO+SrO, 0.001 gram.

The weight of CaO and SrO equals 0.001, from which amount must be subtracted a figure representing the amount of strontium oxide which is soluble in the amyl alcohol used in making the separation. As previously mentioned, 0.0004 gram of strontium oxide is soluble in each 10 c. c. of amyl alcohol; in the above determination 20 c. c. of amyl alcohol were taken, thus necessitating the subtraction of 0.0008 gram from the combined weight of CaO and SrO which gives us 0.0002 gram of calcium oxide, which is equivalent to 0.02 per cent. as one gram of sample was used.

The ether and absolute alcohol method may also be used for this analysis, the results showing the presence of 0.072 per cent. and 0.065 per cent. CaO. The calcium oxide obtained, however, showed the presence of strontium by the flame test and the results were high on that account.

7. MgO.—A trace only of this substance was found.

8. Na_2O.—No material amount of sodium compounds could be found.

ACIDITY (ALKALINITY).

Two-tenths c. c. of standard sulphuric acid were required to neutralize the strontium carbonate in 5 grams of the sample of strontium nitrate. The sulphuric acid used was equivalent to 0.00304 gram of strontium carbonate. This result is reported as strontium carbonate for the reason that an examination of the insoluble portion of the strontium nitrate showed the presence of this compound; it equals 0.061 per cent.

SPECIFICATIONS.

The following specifications are submitted, based upon the investigations made upon the ordinary commercial strontium nitrate:

1. The material shall be white, or at least show only a slight yellowish tinge.
2. The material shall be odorless.
3. When compounded, the material shall be ground so that all will pass through an 80-mesh sieve and 60 per cent. shall pass through a 100-mesh sieve.
4. The material shall contain not less than 99 per cent. of strontium nitrate.

5. The material shall contain not more than 0.2 per cent. moisture when compounded.
6. The dry material shall not contain more than 0.5 per cent. of calcium or magnesium salts or of both together, calculated as oxides.
7. The dry material shall not contain more than 0.5 per cent. of iron compounds calculated as Fe_2O_3.
8. The material shall not contain more than 0.25 per cent. of sodium salts calculated as Na_2O.
9. The material shall contain no free acids.

DISCUSSION OF SPECIFICATIONS.

These specifications are very similar to the requirements set forth for potassium nitrate, and the same reasoning for these specifications may be applied to this salt.

BARIUM NITRATE.

HISTORY.

Barium nitrate was not known until it had been artificially prepared from heavy spar which is barium sulphate. This was known as "barote" from the Greek barys, heavy, and was so named by Guyton de Morveau in 1779 and was afterward called baryta by Lavoisier. The name itself, therefore, is indicative of the great density of its compounds. The older records show that the mineral barite was first investigated by V. Casciorolus, a shoemaker of Bologna, in 1602, who discovered that after ignition with combustible substances it became phosphorescent, on which account it was referred to as Bolognian phosphorus. In 1774 Scheèle found a substance in pyrolusite, a native dioxide of manganese, which gave an insoluble sulphate afterward shown to be identical with that from heavy spar.

Barium occurs principally as the sulphate, barite or heavy spar, which has the formula $BaSO_4$, indicating that it is the barium salt of sulphuric acid. It is generally found associated with metallic ores containing sulphur. Dieulafait has shown that all primary rocks contain barium in sufficient quantity to be easily detected. The oxide of barium (BaO) was first recognized as a peculiar earth distinct from lime by Scheele in 1774.

OCCURRENCE IN NATURE.

As indicated above, barium nitrate does not exist as such in nature. By far the most important source of barium nitrate is barite or heavy spar, which is the sulphate of barium. This mineral is sometimes found with some strontia, silica, clay, etc. It is usually found with metallic ores, especially lead, copper, iron, silver, manganese, and cobalt.

40

The important American localities producing barite are Hot Springs, N. C., Lynchburg, Va., and Washington County, Mo. Tennessee, Connecticut, Kentucky, and Illinois also have extensive deposits. Some barite is imported from abroad, Germany and Hungary both having important mines. Heavy spar is a heavy white or light-colored mineral, vitreous in luster. It occurs in orthorhombic crystals, which are frequently united by their broad sides in crested divergent groups, and vary insensibly from this to masses made up of curved or straight lamellas which are cleavable into rhombic plates. It occurs also in granular, fibrous, earthy, stalactitic, and nodular masses. It has a specific gravity varying from 4.3 to 4.7, and a hardness varying from 2.5 to 3.5. Before the blowpipe, in forceps, it decrepitates and fuses, coloring the flame yellowish green, leaving an alkaline residue. With soda or charcoal it gives sulphur reactions. It is insoluble in acids. It is distinguished among nonmetallic minerals by its high specific gravity, insolubility, and green flame. The white variety is ground and used as an adulterant of white lead and for weighting paper. Colored varieties are sometimes used in ornamental slabs, vases, etc.

Barium is also found in nature in the mineral Witherite, which is the carbonate of barium and has the formula $BaCO_3$. This mineral occurs in veins with lead ores, or in veins of silver on barite, and is probably deposited from solution in water containing carbonic acid. Witherite is not mined in the United States, although small deposits occur near Lexington, Ky., and on the north shore of Lake Superior. The most productive mines are in Fallowfield, England. It has a specific gravity approximately the same as barite and a hardness of 3 to 4. It fuses rather easily before a blowpipe, coloring the flame yellowish green and becoming alkaline. It is soluble in dilute hydrochloric acid with effervescence and is distinguished from barite by this effervescence. It is used as an adulterant of white lead and in refining beet-sugar molasses.

Still another source of barium is the mineral barytocalcite, which is a carbonate of barium and calcium and has the formula $BaCa(Co_3)_2$. This mineral occurs massive and in the form of monoclinic crystals usually of a yellowish-

white color. Barium also occurs in nature in certain silicates as brewsterite, which has the formula $H_4(SrBa)$ $Al_2Si_6O_{16}.3H_2O$; harmotome, which has the formula $H_2(K_2Ba)Al_2.Si_5O_{16}.4H_2O$, and hyalophane or barytafelspar, which has the formula $K_2Ba(Al_2Si_8O_{24})_2$. It also frequently occurs in mineral waters.

METHODS OF MANUFACTURE.

The method for the manufacture of barium nitrate from barite, used at the present time, consists in the roasting of powdered barite with coke, which reduces the barium sulphate to barium sulphide; this being soluble in water is leached out and precipitated as barium carbonate by the addition of soda ash. After being thoroughly washed, the barium carbonate thus formed is dissolved in dilute nitric acid, the solution filtered and evaporated to crystallization. If the work has been carefully done, recrystallization of the product is unnecessary. The sodium sulphide which is formed when barium carbonate is precipitated with the soda ash constitutes a product of wide commercial value.

The mineral barite is not decomposed by boiling with a solution of sodium carbonate as is the case with the corresponding strontium mineral, celestite. Barium sulphate made by precipitation can be so transformed, but this transformation is found to be impossible in case of the mineral barite, although it is identical in chemical composition with precipitated barium sulphate.

AVAILABILITY OF SUPPLY.

There is an unlimited quantity of barite (which is the source for the the manufacture of barium nitrate) available in the United States and England.

PHYSICAL PROPERTIES.

Color.—The salt consists of translucent crystals or a crystalline powder, white in color. The commercial product is slightly yellow, due probably to a small amount of iron salts. It has no odor.

Solubility.—One hundred parts of water at 0° C. will dissolve five parts of barium nitrate; 100 parts of water will

dissolve 34.2 parts at 100° C. The specific gravity of a saturated solution of this salt at 19.5° C. is 1.072.

Hygroscopicity.—A sample of commercial barium nitrate on being dried at various temperatures ranging between 110° C. and 265° C. showed the following results:

At 110° C. the loss of weight was equivalent to 0.07 per cent.

From 110° C. to 265° C. the loss of weight was equivalent to 0.05 per cent.

On exposing a sample to the air for one week which had been previously dried at 265° C., it gained slightly in weight, closely approximating the weight of the original sample.

Flame color.—Beautiful pale-green coloration is the characteristic of pure barium salts of which barium nitrate is an example. A deterioration of this color is found when using the commercial barium nitrate, due to the presence of small quantities of sodium or calcium salts, even though these impurities are present in such small quantities that they can not be detected by ordinary analytical methods. The flame color affected by their presence is evanescent, appearing at the beginning of the test but not after the salt has been in the flame for a short time. This is the same phenomenon as was observed in connection with strontium nitrate.

Fusibility.—Barium nitrate when heated progressively fuses, then decomposes with liberation of nitric fumes and oxygen accompanied by much frothing, leaving a porous mass of barium oxide.

Taste.—A bitter metallic taste is characteristic of soluble barium salts.

Hardness.—It is a comparatively soft compound and is ground easily.

Tenacity and opacity.—It is brittle in nature and translucent.

Specific gravity.—The specific gravity of the salt is 3.24.

CHEMICAL PROPERTIES.

GENERAL NATURE.

The molecular weight of barium nitrate is 261.39. This is made up of barium with an atomic weight of 137.37, 2 atoms

of nitrogen with a total atomic weight of 28.02, and 6 atoms of oxygen with a total atomic weight of 96. It is neutral to litmus and does not change its chemical nature on exposure to the air. The nitrate is the barium salt of nitric acid. It has the formula $Ba(NO_3)_2$, and contains no water of crystallization. In common with other salts of barium it is very poisonous, occasioning first a stimulation of the heart action, followed by paralysis, which is accompanied by muscular spasms. Salts of barium are used medicinally in limited amounts for the treatment of certain tumors and affections of the skin.

REACTIONS.

Like other nitrates previously discussed, barium nitrate owes its efficacy to the fact that the contained oxygen produces great heat when the salt reacts with the oxidizable material that is combined with it in the various pyrotechnic pieces in which it is used. Before the blowpipe on charcoal it fuses easily, deflagrating violently and imparting the characteristic pale-green color to the flame. Like potassium and strontium nitrate, when fused with tungstic anhydride (WO_3) or silica (SiO_2), nitric fumes are evolved, empirically corresponding to N_2O_5. When a solution of this salt is treated with sulphuric acid, a heavy white precipitate of barium sulphate is formed, which is extremely insoluble in water; this is used as a quantitative method for the determination of barium salts.

FUNCTION IN PYROTECHNIC PIECES.

There are two functions which barium nitrate performs in pyrotechnic compositions. The first one is the characteristic green-flame color produced by the barium; the other is to furnish the oxygen in an available concentrated form to support the necessary combustion.

When barium nitrate is used to produce green signals, it is generally combined with barium chlorate. During the decomposition which takes place the barium chlorate becomes barium chloride, which salt is very much more efficient in producing the green coloration than barium nitrate. When barium nitrate is used in mixtures containing no chlorates, the green flame coloration which it produces is relatively

unimportant and is eclipsed by other colors. For example, barium nitrate in connection with metallic aluminum, in the aëroplane flare, produces a light which is almost white, although in foreign practice a small amount of sodium carbonate is sometimes used in connection with the mixture in order that the yellow of the sodium flame may neutralize, to a certain extent at least, the green of the barium. Barium nitrate is superior to any other available oxygen-producing compound for white lights, as the oxide of barium formed during its decomposition is very stable and is not volatilized at the combustion temperature to the extent which the oxides of many other metals are, thus limiting the intensity of the characteristic barium color.

Barium nitrate has been used as a substitute for potassium nitrate in gunpowders, but was abandoned because the barium oxide produced in the explosion rapidly fouls the gun barrel. We find that it is used in connection with potassium nitrate, sulphur and shellac in the aëroplane-flare first fire. Its use in such a composition as the propelling charge for rockets should be quite possible whenever commercial conditions render it economically advantageous.

Green-flame-coloring compositions containing barium nitrate are used for green position lights, such compositions containing barium chlorate, barium nitrate, potassium chlorate, shellac, and stearin, and for green signal lights, where barium chlorate, barium nitrate, and shellac are combined. White lights in which the delicate green of barium is obscured by the extreme luminosity of other materials are the aëroplane flare composed of barium nitrate, aluminum, sulphur, and castor oil, the wing-tip flare and the white rifle light, containing barium nitrate, aluminum, and sulphur; the white position light composed of barium nitrate, sulphur, aluminum, antimony, and stearin, and white signal composition containing barium nitrate, aluminum, sulphur, and saltpeter. Barium nitrate is thus seen to be one of the most important salts for pyrotechnic pieces.

ADVANTAGES.

Barium nitrate has the advantage of being a very cheap product in normal times, with a very large available source

of supply in the United States. The dryness of the salt when exposed to the air, its relatively great safety in handling and its permanency in storage are additional reasons why this salt is of great value. In addition to this, the large percentage of available oxygen which the barium nitrate carries, nearly 37 per cent., makes this salt of great advantage in pyrotechnic compositions. Compare, for example, barium nitrate with potassium nitrate. One c. c. of solid barium nitrate weighs 3.24 grams, containing 37 per cent. of oxygen or 1.2 grams of oxygen. One c. c. of solid potassium nitrate will weigh 2.1 grams, containing $47\frac{1}{2}$ per cent. of oxygen or 1.0 gram of oxygen. Therefore barium nitrate will contain approximately 20 per cent. more oxygen per unit of volume than potassium nitrate.

It is also the only source of green flame producing color which can be prepared in great quantities at low cost. The unique position which barium nitrate occupies in the field of pyrotechnics will no doubt be enlarged and increased as development and research progress.

ANALYSIS.

The following qualitative and quantitative methods for the analysis of barium nitrate are based upon the commercial salt.

QUALITATIVE TESTS.

Flame test.—The test shall be made in the ordinary manner by means of platinum wire moistened with concentrated hydrochloric acid, and dipped in the powdered salt and heated over a Bunsen burner. This test is made for the purpose of determining the purity of the salt in a very general way, in order to indicate the method of procedure.

Acidity.—Ten grams of barium nitrate shall be dissolved in 100 c. c. of previously boiled distilled water. Delicate neutral litmus paper is inserted in the liquor and shall show no acid reaction after an immersion of 15 minutes.

Soluble salts of iron.—Ammonia in excess shall be added to a fairly concentrated solution of the barium nitrate, which has been brought up to the boiling temperature. The presence of

salts of iron is indicated by the formation of a precipitate of ferric hydroxide.

Salts of calcium.—This examination should be made qualitatively as described under the quantitative analysis of the calcium in barium nitrate.

Salts of magnesium.—A solution of barium nitrate shall be treated with an ammoniacal solution of ammonium chloride and ammonium carbonate, whereby barium carbonate is precipitated. This is filtered off and washed and the filtrate treated with a small amount of ammonium phosphate solution and a volume of concentrated ammonia, equal to one-third the volume of the solution, shall then be added. The solution shall be allowed to stand in a cool place for at least 12 hours. The presence of salts of magnesium will be indicated by the formation of a white crystalline precipitate of ammonium-magnesium phosphate.

Chlorides.—To a moderately concentrated filtered solution of barium nitrate, a few drops of nitric acid shall be added, followed by a small amount of a solution of silver nitrate. The presence of soluble chlorides in the material will be indicated by the formation of a white precipitate of silver chloride. Traces will be shown as a turbidity in the solution.

The presence of any material amount of chlorides will indicate that salts of sodium may be found in the original material and serve as a guide for the later quantitative work.

The following results are examples of the qualitative tests made upon a commercial sample of barium nitrate.

Flame test.—The presence of extremely minute quantities of sodium and calcium compounds were shown, although the tests were too evanescent to be convincing in their character.

Acidity.—The salt was neutral.

Soluble salts of iron_____Trace.
Salts of calcium_____Trace.
Salts of magnesium_____Absent.
Chlorides_____Absent.

QUANTITATIVE TESTS.

Moisture.—A weighed sample of 5 grams shall be spread out on a 3-inch watch glass and dried in an air bath at 130° C. to constant weight. The loss in weight thus determined represents the amount of moisture present.

Barium nitrate.—One gram of barium nitrate, which has been dried for the moisture determination, shall be mixed in a platinum crucible with approximately 5 grams of tungstic anhydride (WO_3) prepared by igniting tungstic acid in a platinum crucible with a blast lamp for one hour and subsequently kept in a desiccator over sulphuric acid. The mixture shall then be gradually heated over a Bunsen burner for from 10 to 15 minutes. The tungstate of barium being infusible, the mass will not melt down. The ignition, however, is very quiet, which is insured by a careful preheating of the salt before using until all decrepitation has ceased. The loss in weight is equivalent to the N_2O_5 content of the barium nitrate, and this loss in weight multiplied by 2.4198 will give the weight of the barium nitrate in the sample tested.

Insoluble matter.—Five grams of barium nitrate shall be dissolved in 100 c. c. of boiling distilled water. The solution is then filtered through a Gooch crucible which has been previously dried and weighed. After having been thoroughly washed, the filter flask is changed and the residue washed three times with pure acetone. The crucible is then dried at 100° C. for 30 minutes and weighed. The gain in weight represents the insoluble matter present.

Chlorides.—To the filtrate from the insoluble matter above described, 5 drops of a 5 per cent. solution of potassium chromate shall be added and the chlorides then titrated with a one-fiftieth-normal solution of pure silver nitrate, the end point of the reaction being indicated by the characteristic red color of the silver chromate, which does not appear until all of the chlorides present have been precipitated by the silver nitrate.

Iron.—A solution of 5 grams of barium nitrate in a little water shall be boiled for 15 minutes with 10 c. c. of concentrated nitric acid. After filtering and heating the solution to boiling, a slight excess of ammonia is added and the solution boiled for two minutes. It is then filtered through quantitative paper, the precipitate thoroughly washed with hot water, ignited and weighed. The weight obtained represents the iron content of the material as Fe_2O_3.

Calcium.—The separation of calcium from barium nitrate depends upon the solubility of calcium nitrate in amyl

alcohol and the insolubility of barium nitrate in the same solvent. One gram of the salt shall be dissolved in the least possible amount of hot water in a 150 c. c. beaker, and 30 c. c. of amyl alcohol added, and boiled until the boiling point of amyl alcohol is reached, which is between 128° and 130° C. When this temperature is reached, the volume of the solution will be found to have diminished between one-third and one-half. The water present will have been evaporated and the calcium nitrate will have gone into solution in the amyl alcohol to the exclusion of the barium nitrate, which forms a residue. This is filtered off through a perfectly dry Gooch crucible, which has been previously prepared by washing with amyl alcohol and drying. The beaker shall be rinsed three times with amyl alcohol, passing the wash alcohol through the crucible. The filtering operation should be done in the cold to reduce the solubility of the barium nitrate. The filtrate shall be evaporated to dryness without baking, taken up with water and boiled. The calcium shall be precipitated by ammonium oxalate from an ammoniacal solution to which ammonium chloride has been added. A large excess of ammonium oxalate is required in order to complete the precipitation. On standing over-night the precipitate shall be filtered off and washed with a dilute solution of ammonium oxalate. The precipitate and filter shall then be ignited and weighed as calcium oxide. When small quantities of calcium are present this ignition may be completed in 15 minutes in a platinum crucible.

Magnesium.—Five grams of the material shall be dissolved in hot water and an excess of ammonium chloride and ammonium carbonate shall be added and the solution boiled and filtered. To the filtrate a small amount of a solution of sodium or ammonium phosphate shall be added, followed by one-third of the total volume of the solution in concentrated ammonia. The solution shall then be allowed to stand for 12 hours in a cool place. The precipitated ammonium-magnesium phosphate shall be filtered off, washed with a cold dilute solution of ammonium chloride, ignited and weighed as $Mg_2P_2O_7$.

Sodium.—One gram of barium nitrate shall be dissolved in 5 c. c. of water, placed in a 30 c. c. Erlenmeyer flask and

the sodium precipitated and determined as indicated in the chapter on potassium nitrate.

The following results show an example of the quantitative tests made upon a commercial sample.

Moisture:
                                                    Grams.

   Weight of sample taken_____ 5.000
   Weight after drying_____ 4.9965
   Loss in weight_____ .0035

This loss in weight when divided by the weight taken gives 0.07 per cent.

Barium nitrate:
                                               Grams.

   Weight of silica crucible_____ 13.0517
   Weight of crucible and barium nitrate_____ 14.0588
   Weight of barium nitrate used_____ 1.0071
   Weight of crucible, barium nitrate and WO_3_____ 18.7503
   Weight after fusion_____ 18.3348
   Loss in weight by fusion_____ .4155

When multiplied by the factor 2.4198 and divided by the weight taken we find 99.83 per cent. barium nitrate.

Insoluble matter:
                                           Grams.

   Weight taken_____ 5
   Weight of insoluble matter_____ .0091

This weight divided by the weight taken gives 0.18 per cent.

Chlorides.—Absent.

Iron:
                                              Grams.

   Weight of sample taken_____ 5
   Weight of Fe_2O_3_____ .0013

This weight divided by the weight taken gives 0.03 percent. Fe_2O_3.

Calcium, Magnesium, Sodium.—Absent.

Acidity.—As in the case of strontium nitrate this term might properly be alkalinity as applied to barium nitrate, this condition being caused by the fact that the barium carbonate was not entirely removed from the solution of barium nitrate before the latter was crystallized in accordance with the method of manufacture before stated.

                                              Grams.

   Weight of sample_____ 5
   NaOH equivalent of sulphuric acid required for neu-
     tralization_____ .0026

This amount of NaOH is equivalent to 0.0064 grams of barium carbonate; this divided by the weight taken gives 0.13 per cent. barium-carbonate content.

SPECIFICATIONS.

The following specifications are based upon the investigations made upon the ordinary commercial barium nitrate:

1. The material shall be white or at least show only a slight yellowish tinge.
2. The material shall be odorless.
3. When compounded, the material shall be ground so that all will pass through an 80-mesh sieve and 60 per cent. shall pass through a 100-mesh sieve.
4. The material shall contain not less than 99 per cent. of barium nitrate.
5. The material shall contain not more than 0.2 per cent. moisture when compounded.
6. The dry material shall not contain more than 0.5 per cent. of calcium or magnesium salts or of both together, calculated as oxides.
7. The dry material shall not contain more than 0.5 per cent. of iron salts, calculated as Fe_2O_3.
8. The material shall not contain more than 0.15 per cent. of sodium salts, calculated as Na_2O.
9. The material shall contain no free acids.

DISCUSSION OF SPECIFICATIONS.

Discussing the specifications for barium nitrate as regards the permissible content for sodium salts, it must be borne in mind that barium nitrate is used for two purposes. When used for the production of green lights it is important that the limit of sodium salts should be 0.15 per cent., as above indicated. If, however, the barium nitrate is to be used for the purpose of creating white lights, the presence of slight impurities of sodium salts is rather an advantage than a disadvantage, for sodium salts are sometimes added to obscure the barium green when compounding white-light mixtures.

SULPHUR.

HISTORY.

The word sulphur is derived from the ancient Sanskrit, meaning literally "The enemy of copper," the ancients having the idea that the metallic qualities of silver, gold, and copper ennobled them among the metals, and that anything that would tend to do away with these metallic properties, as sulphur does when melted with copper, was to be regarded as their enemy. The word has come down to us through the Greek and Latin almost in its present form. Sulphur and mercury were regarded by the alchemists as the father and mother of the other metals, their idea being that all metals could be produced by combining sulphur with mercury in different proportions and under different mystic conditions. In the age of Iatro or medical chemistry that followed that of alchemy, sulphur also played an important part. This importance may really be ascribed to the fact that the material was of common occurrence and could easily be obtained. The first gunpowder, a sulphur, saltpeter and charcoal mixture, was undoubtedly discovered by accident, for the lack of accurate knowledge of the properties of the ingredients would render any other explanation improbable. It is certain that the early pyrotechnic compositions made use of the properties of the element. Further, its use as a constituent of gunpowder must be regarded more as the result of a gradual development than as the invention of any one person.

OCCURRENCE IN NATURE.

Native sulphur occurs in large deposits in various parts of the world. The great foreign sulphur-producing region is the island of Sicily. Deposits are numerous in the United States and have been developed at Cove Creek, and Fresno, Utah; and Winnemucca, Nev.; extensive deposits are also

52

known in California, Louisiana, Wyoming, and Texas. It is found in large quantities in Mexico, there being unusually large deposits in the Volcano Popocatepetl from which the Spaniards under Cortez obtained a supply for gunpowder during their conquest of the country. It is also found in quantities in South America, Iceland, Japan, Asia, New Zealand, and other parts of the world, and some of these places constitute valuable sources of supply. It sometimes carries traces of tellurium, selenium, and arsenic; it is often mixed with clay or bitumen. It is generally found in the free state in the neighborhood of volcanoes, active and extinct, and is a characteristic product of volcanic action. Sulphur also occurs as the sulphides of various metals, such as iron, copper, lead, zinc, etc., which are extremely important for both their metal and sulphur content. The most important examples of such minerals are pyrite, chalcopyrite, galena, sphalerite, mispickel, etc.

Deposits of free sulphur occur in sedimentary rocks as a product of bacterial action, certain bacteria, the anærobes, having the property of reducing sulphates. Combined with oxygen and bases, sulphur is found in nature as gypsum and anhydrite, which are sulphates of calcium similar to heavy spar which is the sulphate of barium; and celestite which is the sulphate of strontium; as Epsom salts and kieserite, which are the sulphate of magnesium.

Sulphur is also found in nature combined with hydrogen, as hydrogen sulphide, or sulphureted hydrogen, and occasionally with carbon and oxygen as carbon oxysulphide in a number of mineral waters, which are supposed to owe their therapeutic value to such sulphur compounds.

Sulphur is found combined in vegetable and animal tissues in a variety of proteid substances; it is found in hair, nails, and horns. Many volatile oils, such as oil of mustard and oil of garlic, are composed of organic-sulphur compounds to which their characteristic smell and other properties are due. At the present time the two principal sources of supply are the island of Sicily, and Louisiana in the United States. The commercial crude Sicilian sulphur which constitutes a very large proportion of the sulphur trade contains impurities ranging in amount from about 2 to 11 per cent. It is known as Greggio, and its

price varies according to the amount of impurities. Thus
it is graded as "Best unmixed seconds," "Best unmixed
thirds," and "Current thirds." These three grades prac-
tically represent the entire Sicilian brimstone trade. If
pure sulphur is required from these grades, it is prepared
by refining, and as a result the impurities of the commercial
refined product are reduced to about one-half of 1 per cent.
It is then sold as raffinate. The sulphur in the Sicilian de-
posits occurs in Miocene strata and constitutes what is
known as the "Gypsum type," as distinct from the "Sol-
tafara type." Marl, shale, and gypsum are prominent con-
stituents of the sedimentary rocks in which the sulphur is
contained. The reducing action of the bituminous matter
under the proper conditions of temperature and pressure
upon gypsum results in the formation of calcium sulphide,
which in turn is acted upon by oxygen, carbonic acid, and
moisture, producing calcium carbonate, sulphureted hydro-
gen and poly-sulphides of lime. The later in turn yield
calcium carbonate, sulphur, and sulphureted hydrogen.

It is stated by Fuchs and De Launay that 24 per cent. of
the sulphur represents about the average that would be
deposited as the result of these reactions, and inasmuch
as this percentage may be taken as representing the average
amount of crude sulphur found in Sicilian sulphur rock, it
is regarded as a strong argument in favor of the sulphur
being deposited in the manner suggested. The mines are
distributed throughout the provinces of Caltanisetta and
Girgenti. They cover an area of about 100 by 55 miles.
The deposits of sulphur (solfare) vary in depth from 150
feet to about 650 feet, and in the deep mines the ore is now
all brought to the surface by mechanical means; in the past,
it was practically all mined by manual labor.

The effect of the Louisiana sulphur competition upon
Silician production may be strikingly illustrated by the
fact that in the year 1903 there were 757 active sulphur
mines in Sicily and that nearly 40,000 operatives were em-
ployed. In 1913 the number of mines being worked was
about 400 and the number of operatives about 20,000. The
great deposits of sulphur in Louisiana are geologically asso-
ciated with "dome formation" which constitutes a striking
feature of the Costal Plains extending through the States

of Louisiana and Texas and the Gulf States of Mexico. These deposits were first found in 1865. The Louisiana Oil Co. located them when drilling for oil in the head of Bayou Choupique, about 15 miles west of Lake Charles, at a depth of 443 feet. It was proved that this sulphur bed had a depth of about 100 feet. Further detailed examination showed that the sulphur deposits have an average overburden of about 464 feet, consisting of about 376 feet of clay and sands, Pleistocene quicksand and gravel, Port Hudson and Orange Sand Groups, and about 88 feet of soft rock, mainly gray limestone. The average depth of the sulphur bed is 125 feet; beneath the sulphur is gypsum with occasional layers of sulphur. The Louisiana deposits, owned by the Union Sulphur Co., practically supply all the sulphur obtained in the United States. Endeavors have been made and are still being made to locate other deposits in the same geological formations.

METHOD OF MANUFACTURE.

The Frasch process may fairly be described as one of the triumphs of modern technology and the result of its successful development has been to provide a great industry for the United States which it did not previously possess and to remove from Sicily to this country the domination of the conditions regulating the world's supply of sulphur.

Herman Frasch, who had long been engaged in industrial research work in the United States in connection with petroleum drilling and refining, heard in 1891 of the difficulties connected with the mining of Louisiana sulphur. As a recult of prolonged study he arrived at the conclusion that the ordinary mining methods were inapplicable, but that the problem could be solved provided he could introduce superheated water into the sulphur bed through a tube passing through the quicksand at a temperature above the melting point of sulphur, and then raise the molten sulphur through another tube to the surface. The molten sulphur would then solidify on cooling at the surface; the sulphur thus obtained would necesarily be of high purity. To succeed with this scheme meant not only to overcome difficulties in connection with lateral pressure upon the tube already alluded to, diffi-

culties in introducing the superheated water to the sulphur about 500 feet below the surface at the required temperature, but also difficulties due to the pool or well of the melted sulphur formed below the bottom of the tube by this superheated water, and difficulties in raising this molten sulphur from the pool or well to the surface before it could be cooled below the melting point by the incoming water from the quicksand. For this purpose, with his associates, he acquired the property in the name of the Union Sulphur Co., Cleveland, Ohio. It consisted of a flat-lying area of 5,000 acres situated near the Parish of Calcasieu, La., 80 miles from Port Arthur, Tex., on the Gulf of Mexico, and 288 miles from New Orleans, La. The property is about 50 miles east of the great Texas oil fields, at Beaumont, and is geologically the eastern extension of that field.

To carry out this process the pumping was done by an "air lift" by means of which the molten sulphur was forced through a tube to the surface. The advantage resulting from the use of the compressed air is that the specific gravity of the mixture of air and sulphur which is raised is lower than that of the molten sulphur by itself, and hence the strain upon the great length of pipe is reduced. The mixture employed is two parts by volume of air to one part of molten sulphur. A well 17 inches in diameter is bored to a depth of some 50 feet. This is not provided with a casing, but a mixture of clay and water is pumped down with a view to filling up the interstices in the sand, whereby caving is greatly reduced. Within this well a wrought-iron pipe 13 inches in diameter is sunk to a variable depth, dependent upon outside pressure. Sometimes it can be arranged to reach the bottom of the quicksand at about 250 feet. A mixture of clay and water is employed in connection with this pipe, and in addition to helping to support the walls, it materially facilitates the withdrawal of the pipe when the well is exhausted, thereby effecting a considerable economy in the working of the process.

Inside this 13-inch-diameter pipe an 8-inch-diameter pipe is driven to the bottom of the sulphur bed. Water and clay are also used. Those sections of the pipe which are intended to be in the sulphur bed are perforated with holes of ½ inch diameter arranged in spiral form, the holes being 6 inches

apart. This arrangement is intended to prevent gypsum, etc., getting to the bottom of the pipe. The superheated water which is conveyed through this pipe to the sulphur bed has free access to the sulphur throughout the entire thickness of the deposit, and any substance which should by chance get into the bottom of the pipe causes no trouble. Inside the 8-inch-diameter pipe an unperforated 6-inch-diameter pipe is sunk to the bottom of the sulphur bed. Superheated water is also pumped down this pipe. Inclosed in this 6-inch pipe is an unperforated 3-inch-diameter pipe through which the molten sulphur is raised to the surface. Inside this 3-inch pipe is driven to the bottom of the bed a 1-inch-diameter unperforated pipe through which the com- · pressed air is forced.

Superheated water is pumped down the 8- and 6-inch pipes. The water from the 8-inch pipe melts the sulphur which (specific gravity 2.06) sinks down alongside the pipe to the bottom of the sulphur bed. The water in the 6-inch pipe mainly serves to keep the sulphur hot in the inclosed 3-inch pipe, thereby preventing crystallization on its way to the surface. Compressed air at a pressure of 250 pounds per square inch is forced down the 1-inch pipe to raise the sulphur by the "air lift." This pressure is found sufficient in practice to raise the sulphur to the surface, as the air is helped by the head of water in the 6- and 8-inch pipes to overcome the weight of sulphur in the 3-inch pipe.

Sawdust is introduced with superheated water once the pool of liquid sulphur has been formed. This prevents to a very great extent the flow of quicksand water into the pool with consequent lowering of temperature. The steam pressure runs at about 100 pounds. It has been estimated that of the total heat units employed, one-half of 1 per cent. only are utilized in melting the sulphur. The temperature of the quicksand water, of which there is a great influx to the sulphur bed during the operating of the process, is low and has to be raised before the sulphur can be melted. The well gives out when the cavity from which the sulphur has been extracted becomes too large to permit of the necessary temperature being maintained. On reaching the surface the sulphur is conducted through a pipe to a bin in which it quickly solidifies. In order to remove the sulphur from

the bins to the railway trucks, the roughly constructed wooden framework is removed and blasting applied to the bottom of the sulphur. In this way the sulphur on being shot down by the blasting is so broken up that it can be picked up by grab buckets, which by means of cranes discharge it into wagons at such a speed that a 35-ton wagon can be filled in about 14 minutes. The sulphur obtained by the Frasch process is of a very high degree of purity, from 99.93 to 99.98 per cent., and in addition only contains a trace of water. The process is only applicable when the deposit is exceptionally rich in sulphur—say between 60 and 70 per cent.—and for this reason among others it is not available for use in Sicily.

Other methods for the mining and extraction of sulphur have been used since the time sulphur became known to the ancients, discussions of which do not properly come within the province of this book.

The sulphur for pyrotechnic uses is purified by a still further process of distillation. In distilling the crude sulphur produced as outlined above, it has been found that it will partly sublime and partly distill over as a liquid, consequently the still is arranged with a chamber to catch the sublimed product and a side delivery tube in which the liquid condenses. The sublimed sulphur, known to the trade as " Flowers," is found to contain free acid, and on that account is undesirable for pyrotechnic compositions. The molten product, however, after it has solidified, does not contain this free acid, and when ground is the sulphur used for the various compositions for pyrotechnic purposes. This is known as " Flour " of sulphur. A peculiarity of this grinding is that the fineness of the product has a very marked influence upon the density.

AVAILABILITY OF SUPPLY.

Sulphur is one of the articles indispensible for pyrotechnic uses which may be produced and is being produced in any desired quantity within the limits of the United States. As a result of many tests it is estimated that the Louisiana deposits contain not less than 40,000,000 tons of sulphur, and that it would be a conservative estimate to conclude that

not less than one-half of this quantity could be brought to the surface by the Frasch process. Doubtless many of the other American deposits mentioned could be developed if necessary to produce additional enormous quantities at a cost which would be well within economic limitations. It has been estimated that the Mexican sulphur from the crater of Popocatepetl could be mined and delivered to New York City at a total cost not exceeding $10 per ton. It is certainly the cheapest and most available material of any of those used for pyrotechnic purposes.

USES OTHER THAN IN PYROTECHNICS.

Sulphur is used in the manufacture of sulphuric acid, in the paper industry, in the vulcanizing of rubber, as a constituent of certain cements, in the manufacture of carbon disulphide, artificially made sulphides, hyposulphites, in the bleaching of silk and wool by means of sulphur dioxide, in the manufacture of ultramarine, artificial vermilion, and in the making of enamels. Another important use of sulphur is in combination to make insecticides to prevent the growth upon grape vines of the microscopic mold fungus, to prevent the growth of mold on hops, and very many other practical purposes. As has been said it is an important constituent of gunpowder and other explosives. It is used also in matches and has in addition distinct medicinal value.

PHYSICAL PROPERTIES.

Several allotropic varieties of sulphur are known, characterized by differences in crystalline form, specific gravity, behavior toward solvents, etc. For pyrotechnic purposes, however, the flour of sulphur only will be considered.

Color and odor.—It is yellow in color and has a characteristic odor.

Solubility.—Sulphur is insoluble in water and only slightly soluble in alcohol, ether, and ethereal oils. In carbon bisulphide it is soluble to the extent of about 40 per cent. in the cold, and about 182 parts will dissolve in 100 parts at 55° C., which is the boiling point of the saturated solution.

Sulphur dissolves freely in benzyl chloride. The solubility increases from 1 per cent. at 0° C. to 55.8 per cent. at

134° C. It melts in benzyl chloride at 106.2° C. to 106.8° C., and does not mix with the excess of solvent, but above 136° C. it mixes with benzyl chloride in all proportions. It is soluble in light petroleum. Benzene and toluene dissolve about 26.4 parts at 100° C. Tar oil dissolves about 50 per cent. at 100° C.

Hygroscopicity.—It is nonhygroscopic.

Flame color.—It does not impart any color to flame.

Fusibility.—The melting point of sulphur (prismatic crystals) is 120° C. It boils at 444.6° C. Before arriving at the boiling point, molten sulphur passes through several modifications. When first melted it forms a light-yellow clear mobile liquid. On raising the temperature this liquid rapidly becomes thick and viscous and dark in color, and if the temperature is still further elevated the liquid again becomes mobile, but does not lose its dark color.

Taste.—Pure sulphur is practically tasteless.

Hardness.—It is very soft and friable. It has a hardness of 1½ to 2½.

Tenacity and opacity.—It is brittle and translucent.

Specific gravity.—The specific gravity is 2.06.

CHEMICAL PROPERTIES.

GENERAL NATURE.

The atomic weight of sulphur is 32.06, and it has the chemical symbol S. It is neutral to litmus and does not change its chemical nature on exposure to the air. It carries no water of crystallization and is nonpoisonous. Chemically it is a reducing agent combining readily with the oxygen of the air or with the oxygen of the oxidizing salts used in pyrotechnic practice.

REACTIONS.

It melts easily, then takes fire, and burns with a blue flame, producing the suffocating odor of sulphur dioxide. In a closed tube it melts and yields a fusible sublimate, brown when hot, yellow when cold. If rubbed on a moistened silver coin the coin is blackened.

FUNCTION IN PYROTECHNIC PIECES.

Sulphur has two functions in pyrotechnic compositions. It serves first as a fuel to be oxidized by the available oxygen contained in the other constituents; and, second, it acts as a deterrent, wnere otherwise the process of combustion would be too rapid. It is of advantage in that it does not influence the color of the flames produced.

ANALYSIS.

The following quantitative methods for the analysis of sulphur are based upon a commercial sample.

Moisture.—A weighed sample of about 5 grams shall be spread out on a 3-inch watch glass and desiccated to constant weight over sulphuric acid.

Acidity.—A weighed sample of approximately 10 grams shall be treated with 100 c. c. of neutral distilled water heated to boiling for 2 minutes with constant stirring, filtered and the filtrate titrated with standard alkali. The acidity shall be reported in terms of sulphuric acid, H_2SO_4.

Ash.—Ten grams shall be burned in a weighed porcelain or silica crucible, under a hood. The residue shall then be ignited and weighed. The weight of the residue shall be reported as ash.

EXAMPLE.

Moisture:

	Grams.
Weight of sample taken	5
Weight after drying	4.9996
Loss in weight	.0004

This divided by the weight taken gives 0.008 per cent.

Acidity.—One drop of one-twentieth-normal caustic-soda solution being sufficient to give an alkaline reaction when added to the filtrate, no acidity was reported.

Ash:

	Grams.
Weight of sample taken	10
Weight of ash obtained	.0022

This divided by the weight taken gives 0.02 per cent.

Sulphur.—Determined by difference. The determination was found to be 99.97 per cent.

SPECIFICATIONS.

Sulphur for use in military pyrotechnics shall be in accordance with the following specifications:

1. The material shall be what is known as heavy flour of sulphur (not flowers).
2. The dry material shall contain at least 99.9 per cent. sulphur.
3. The dry material shall contain not more than 0.02 per cent. of acidity, calculated as H_2SO_4, at the time of mixing the composition.
4. The material shall not contain more than 0.2 per cent. of moisture.
5. The material shall be ground so that 89 per cent. or more shall pass through a 150-mesh sieve and all through a 120-mesh sieve.

· CHARCOAL

HISTORY.

The first part of the word charcoal is of obscure origin. The independent use of "char," meaning to scorch or to carbonize, is comparatively recent and must have been taken from "charcoal" which is the word the English Dictionary gives as the earliest instance of the use of "char" in a quotation dated 1679. No suggestions for the origin of the word "char" are satisfactory. It may be an adaptation of the word "chore" meaning a turn of work, and charcoal would have the meaning "turned coal," i. e., wood that has been changed or turned to coal. This is a somewhat forced derivation for which there is no authority. Charcoal was known to the ancients and was prepared and used by the Egyptians.

OCCURRENCE IN NATURE.

Charcoal rarely occurs in nature, except when it is accidently formed by forest fires and the like, in which cases it is usually found in a partially carbonized condition. It is found in nature, however, combined with hydrogen, in coal, bitumen, shale, naphtha, the paraffins, and numerous other hydrocarbons; with oxygen it is found as carbon dioxide, which occurs in large quantities and which forms the large class of metallic salts called carbonates. In the vegetable kingdom the dry solids contain nearly 50 per cent. of carbon, while all animal matter is largely made up of fat, containing as much as 79 per cent. of carbon. Occasionally, also, it is found in veins of coal, particularly in those of recent geologic formation.

METHOD OF MANUFACTURE.

Charcoal is made from wood. At one time the charcoal for black powder was made almost exclusively from alder

wood, but later other soft woods were used and straw charcoal was also introduced into the brown powders for heavy ordnance. The better qualities of gunpowder are generally made with charcoal which has been prepared from soft woods, on account of the fact that it burns more easily. Dogwood is used considerably in England, especially for small-grain powders, which are used when rapid burning is desired; alder and willow are used for larger-grain powders. In Austria and Germany alder, willow, and hazel woods are used; in Switzerland hazel wood; black alder is used for high-class powders in France and common white woods, such as white alder, poplar, aspen, birch, and hazel wood, are used for mining powders; oleander, yew, willow, hemp stems, and vine woods are used in Spain; hemp stems are used almost exclusively in Italy.

When charcoal is made by burning in heaps or kilns, it has been found to be undesirable for the manufacture of gunpowder, because the burning can not be done uniformly, and it was found to be necessary to select the wood very carefully in order to secure the desired results. It has, therefore, been deemed expedient to prepare charcoal for gunpowder and for use in pyrotechnics by heating the wood in ovens or iron vessels. The practice of to-day does not differ materially from that used in the fourteenth century. The wood should be cut in the spring as the sap at that time of the year contains much less inorganic matter; the percentage of ash in such woods will therefore be much smaller, although the proportion of sap is larger. In addition to that, such wood is freed more easily from its bark; the bark is undesirable as it contains a large proportion of ash. It is customary to store the wood for from 18 months, minimum, to 3 years, which permits the sap to dry out of it and other changes to take place. The practice of storage varies in different localities, depending upon climatic conditions. At Dresden it is kept in sheds; in Spandau in the open; it is also kept in the open at Waltham Abbey, but the dogwood is covered with thatch, whereas the alder and willow are not so covered. The wood is split if necessary, into pieces about 1 inch thick and these are placed in iron cylinders about 2 feet in diameter and 3½ feet long. By means of suitable tackle these cylinders are raised and

placed in a furnace which is heated as uniformly as possible. The higher the temperature and the longer the heating, the lower is the percentage of hydrogen and oxygen in the charcoal and the greater is its hardness and the difficulty with which it is ignited. Depending upon the particular kind of powder desired, charcoal is heated from four to eight hours.

When the temperature of the wood attains about 280° C. volatile products of decomposition come off in volume. Acetate of lime and wood spirits may be prepared from the condensation of these volatile products. This is not usually done however, where charcoal is prepared for use in powder mills, on account of the fact that at such places the charcoal plant is comparatively small, while the charcoal-producing plants for metallurgical processes are very much larger. It is therefore customary to use these volatile products as fuel by returning them into the furnace by which the wood is being heated, thus economizing fuel. Holes are bored at the ends of the iron cylinders to permit the gases and volatile products to escape, and by means of a pipe these volatile materials are carried away. The end of the process of carbonization is indicated by the color of the flame of the burning gases. This is a characteristic blue color. The furnaces are then opened, and by means of tackle the cylinders are removed and fresh cylinders of wood are put in immediately, before the furnace has had time to cool. The removed cylinders are placed inside of larger cylinders which have closely fitted lids and there allowed to cool. The air must be carefully excluded in this cooling process as the charcoal will otherwise catch fire. The absorbent qualities of charcoal are so great that even when cold it may absorb such large quantities of oxygen from the air that the heat developed may be sufficient to ignite it. It is therefore necessary that the access of the air to the charcoal should be gradual; a week should elapse after it has been burnt before the charcoal is ground. Before it is used the charcoal is carefully picked over by hand in order to remove any material which has not been properly burnt, as well as any foreign matter which may have gotten into it. The charcoal for pyrotechnic purposes should be jet black. When broken it should show

a clear velvetlike surface; it should be light in weight and sonorous when dropped on a hard surface, and so soft that it will not scratch polished copper. The yield of such charcoal is about 30 per cent. by weight of the dried wood.

AVAILABILITY OF SUPPLY.

The supply of charcoal is limited only by the amount of wood which can be grown for this purpose. Its cost is small compared with most of the other products used in pyrotechnics. Charcoal may be made in any part of the world as wood exists everywhere to a greater or less extent.

USES OTHER THAN IN PYROTECHNICS.

Its use as a fuel in metallurgical processes is probably its greatest value, although it has been largely supplanted by coke and coal. Perhaps its next most important use is as an absorbent of coloring and other organic matters in filtration processes, in order to purify the various substances. This is a selective action of charcoal and is used in many ways, the most important of which is the decolorization of sugar solutions. Charcoal has the valuable property of acting as a reducing agent on account of its affinity for oxygen, although its use as a reducing agent in chemical processes has been largely replaced by coke and coal on account of its low crushing strength and the great rapidity with which it burns. It has more limited use in the fine arts and in numerous small operations. It is used as a medicine to a limited extent.

PHYSICAL PROPERTIES.

Color.—It is black in color and has a characteristic submetallic luster.

Solubility.—Charcoal is insoluble in hot and cold water.

Hygroscopicity.—It is fairly hygroscopic and has in addition the property of absorbing large quantities of gases.

Flame color.—Charcoal imparts no color to the flame although it may be easily burned.

Fusibility.—It is infusible and nonvolatile, but signs of volatilization are apparent in the electric arc.

Taste.—It has no taste.

Hardness.—It is very soft and easily ground.

Tenacity and opacity.—It is friable and opaque.

Specific gravity.—Exclusive of pores it has a specific gravity of 1.5 to 2; inclusive of pores, soft charcoal has a specific gravity of 0.2 to 0.36, and hard charcoal, inclusive of pores, has a specific gravity of 0.35 to 0.5.

ABSORPTION PROPERTIES.

The property of charcoal to absorb gases to an extraordinary degree is not only a most remarkable property in connection with pyrotechnics, but has distinct commercial value as well. Its use in the canteens of gas masks to absorb gases has rendered protection against gas warfare possible. During the progress of the War the Gas Defense Section developed varieties of charcoal having the power of absorbing far greater volumes of gas than the charcoal prepared in the ordinary manner. According to Saussure, 1 cubic inch of charcoal, obtained from dense forms of wood such as boxwood, absorbed:

	Cubic inch.
Ammonia gas	90
Sulphureted hydrogen	55
Ethylene	35
Carbon monoxide	9.42
Oxygen	9.25
Nitrogen	6.5

This absorption is very rapid at first, but gradually decreases and is very much influenced by temperature. One cubic inch of charcoal made from cocoanut will absorb 171.7 cubic inches of ammonia gas, but only 17.9 cubic inches of oxygen. The oxygen absorbed from the air by freshly prepared charcoal is in a highly active condition and for a certain space of time can be utilized for the destruction of oxidizable gases, but after being kept for a long time the oxygen by contact with the carbon gradually becomes converted into carbon dioxide. Finely powdered charcoal sprinkled over decomposing animal matter absorbs the gases evolved and oxidizes them by virtue of the condensed oxygen in its pores, and for this reason it is largely used in the construction of sewer traps and respirators.

CHEMICAL PROPERTIES.

The atomic weight of charcoal is 12.005. It is an element and an allotrope of carbon. It does not change its chemical nature on exposure to the air, although it absorbs moisture and large volumes of gases when so exposed. It usually carries from 3 to 4 per cent. of ash.

CHEMICAL REACTIONS.

This substance is one of the most stable known, in that it is not acted upon by acids or alkalies. Its most useful property in connection with pyrotechnics is its function as a fuel, furnishing the burning material. It burns to carbonic-acid gas or carbon dioxide, having the formula CO_2, and when this gas comes in contact with additional amounts of hot charcoal, carbon monoxide, having the formula CO, is formed, consequently the products of combustion of pyrotechnic compositions, including charcoal, will often contain both carbon monoxide and carbon dioxide.

The spontaneous ignition of charcoal in connection with the subject of pyrotechnics is a matter to which considerable attention might properly be attached. When the charcoal absorbs the gases with which it comes in contact, a great amount of heat is developed. At first this absorption is purely mechanical and itself causes a rise in temperature. This makes it necessary to permit the access of the air very gradually after the charcoal has been prepared and allowed to cool, otherwise spontaneous ignition would take place. The rate of absorption varies with the amount of surface exposed, so that when charcoal is finely powdered, the exposed surface being much greater, absorption becomes more rapid and a rise in temperature at once takes place. If after it has been made, charcoal is kept for a day out of contact with air and is then ground down into a powder, it will frequently fire after exposure to the air for 36 hours, while a heap of charcoal powder of 100 bushels or more will nearly always ignite.

It is self-evident that the more porous a body is the greater amount of exposed surface will be available for the condensation of gases, and the great power which charcoal has of absorption is undoubtedly due to its great porosity. The

temperature at which wood can be carbonized varies very considerably, as wood will begin to char at a temperature very little above that of boiling water. In the manufacture of some kinds of gunpowder the charcoal is formed by heating with superheated steam. Charcoal formed at this temperature, however, still contains large quantities of hydrogen and hydrocarbons and is not nearly so porous as charcoal made at a high temperature, although the diminution in porosity makes it less susceptible to spontaneous combustion due to the heat produced by the condensation of gases. When a substance absorbs oxygen the gas is in a very chemically active condition and will set up chemical combinations with considerable rapidity. If charcoal be burned at a high temperature the carbon is in a dense condition and resists to a considerable extent the setting up of chemical action by the oxygen absorbed in its pores; but if it has been formed at a low temperature, this absorbed oxygen will rapidly act upon the hydrocarbons and hydrogen still remaining in the mass, and will raise in this way the temperature to a dangerous point. It is probable that very many unexplained fires have been brought about by beams and woodwork becoming charred in contact with flues and heat pipes.

It has been experimentally determined that when wood has been carbonized at 500° C. it will take fire spontaneously when the temperature is raised in the presence of air to 680° C., and that when wood has been charred at 260° C. a temperature of 340° C. only is required for its spontaneous ignition. If a beam is in contact during the winter months with a heated flue or even steam pipes, it becomes carbonized upon its surface, and during the summer when the flue or pipe is not in use it absorbs air and moisture, and during the next winter it again becomes heated and further carbonized, at which time moisture and air are driven out, leaving the pores in a condition eminently adapted for the absorption of more air as soon as the temperature is allowed to fall. In some cases sufficient heat is generated to cause the charred mass to smolder and when air is freely admitted to it, to burst into flame. In the case of charcoal made at a high temperature it may be taken that the cause of heating is largely physical, while in the case of charcoal made at a low tem-

perature it becomes chemical as well as physical, and it is this chemical action which is the most dangerous, and accounts in most cases for spontaneous combustion.

FUNCTION IN PYROTECHNIC PIECES.

Charcoal is part of the composition of the propelling charge of rockets, of the various fuses and quick matches used, and also some of the priming mixtures. Further, as ordinary gunpowder, it is used in the expelling charge of rockets, aëroplane flares, and some other pieces. Concerning the rocket propelling charge, attention is drawn to the fact that the proportions of saltpeter, sulphur, and charcoal used for this purpose are entirely different from those used in gunpowder.

What is required is a slow-burning powder, not one that will explode. This result is attained by reducing the percentage of saltpeter and increasing the percentages of sulphur and charcoal. This result is further attained by the use of a coarser charcoal than is used in ordinary gunpowder. Ordinary black powder is composed of:

	Per cent.
Saltpeter	75
Sulphur	10
Charcoal	15

while in the rocket-propelling charge the composition is:

	Per cent.
Saltpeter	54
Sulphur	13.4
Charcoal	32.6

This produces a very much slower-burning composition. The fuse or match compositions are slow in their burning, owing to the fact that the powder is disseminated throughout the fiber of the twine used in making the body of the fuse. In all these compositions the charcoal plays the part of the reducing agent or fuel which is consumed by the available oxygen of the saltpeter. The gases produced during the combustion afford the propelling power desired. As to the composition of the gases produced, reference is made to the chapter on potassium nitrate. It should be noted that the gases and moisture occluded or absorbed by the charcoal will

have their effect when liberated by the combustion of the charcoal during the functioning of the piece. It is the practice of the manufacturers of pyrotechnic pieces to mix the potassium nitrate, sulphur and charcoal themselves by hand in the proportions desired for the rocket propelling charge. Doubtless more uniform results could be attained if this blending was done by the approved methods of the black-powder manufacturers.

METHOD OF ANALYSIS AND DISCUSSION OF SPECIFICATIONS.

While there is no difficulty which presents itself in the analysis of the charcoal used in pyrotechnic compositions, the difficulty of establishing specifications for charcoal soon becomes apparent. It is hard to make specifications which shall set forth the percentage of moisture which may be present or the amount of volatile combustible matter, or fixed carbon, or the amount of ash which such charcoal should carry, and be fair to the manufacturers of this product, as the range in various woods is such as to make it impracticable.

The physical examination of the product should be the principal guide and in connection with this it should be observed that the material should not be moist and that it should carry no foreign matter to any appreciable extent; that it should be jet black in color, showing that it has been completely carbonized, and that it should carry not more than the usual amount of ash. It is impossible to set any limit on the amount of ash which charcoal should contain, as this factor varies with the kind of wood from which it is prepared. Of the tests which should be made for the above examination, the determinations of moisture and of any foreign or gritty or metallic substances only need special mention. The moisture shall be determined on a 3-gram sample spread on a watch glass and dried in an air bath at 105° C. for one hour, cooled in a desiccator and weighed immediately. Foreign matters, and gritty and metallic substances are determined by taking approximately 1 gram and stirring it with 50 c. c. of cold water in a beaker, when an observation should be made immediately, noting if any appreciable quantity of such foreign substances settles on

the bottom of the beaker. The determinations of volatile combustible matter, fixed carbon, and ash may be made in the same way as is done in the analysis of coal. It is important that the charcoal for pyrotechnic purposes shall be free from sand, dust, and metallic particles, as these would contribute an element of danger during the compression to which the charcoal is subjected when made up into the various pyrotechnic pieces in which it is used. These foreign particles pressed together might produce enough heat by friction to cause the spontaneous ignition of the composition.

ANALYTICAL RESULTS.

Moisture.—Four different samples of charcoal show the following results:

No.	Brand.	Grain.	Percentage moisture.
1	No. 4 charcoal..................	Medium coarse..........	2. 55
2	No. 10 charcoal.................	Very coarse............	3. 21
3	D. C. XX.....................	Fine powder...........	3. 27
4	No. 20 charcoal.................	Medium coarse........	3. 54

Ash.—No. 4 charcoal (medium-coarse grain) shows an ash content of 3. 37 per cent.

The samples on examination with a hand-magnifying glass showed no trace of incomplete carbonization, which would be shown by the appearance of brown particles, and there was no evidence of any sand, dirt, or metallic particles when the samples of charcoal were stirred with water as indicated.

SPECIFICATIONS.

As already discussed, specifications for charcoal will of necessity offer considerable latitude.

1. Charcoal should be black and should not exhibit more than a reasonable amount of brown particles indicative of incomplete carbonization.
2. The ash shall not exceed an amount proportional to the ash of the wood from which it is prepared.
3. The moisture content shall not exceed 5 per cent. when compounded.
4. The charcoal shall be reasonably free from all grit, sand, and foreign substances of a gritty nature. Traces of the above cannot be avoided; however, the amount of grit and sand must not exceed a reasonable figure for the reasons previously outlined.

CHAPTER VI.

STRONTIUM CARBONATE.

HISTORY AND OCCURRENCE IN NATURE.

As has already been mentioned in the chapter on strontium nitrate, strontium carbonate occurs in nature as the mineral strontianite. So far as known, however, this mineral does not exist in a sufficiently pure condition to permit of its direct use, being invariably contaminated with foreign substances. The principal impurity found in the native mineral is calcium carbonate. This calcium carbonate affects the color of the flame to such an extent that the native mineral cannot be used, and consequently the strontium carbonate to be used for pyrotechnic purposes must be a manufactured article.

METHODS OF MANUFACTURE.

There are two methods of producing strontium carbonate which have been used in commercial practice; as this substance is necessary for the production of strontium nitrate, these methods have already been dealt with in the chapter treating with the latter compound. It is essential, however, to call attention to one vital difference. In manufacturing strontium nitrate, strontium carbonate is dissolved in nitric acid. The nitrate formed is purified by crystallization, which affords a very easy method of getting rid of the foreign substances which might have been present in the carbonate. Strontium carbonate, being an insoluble compound, cannot be purified by crystallization, and consequently the impurities which are permissible in a strontium carbonate subsequently to be used for making the nitrate would prevent the use of the crude carbonate itself. The process of crystallization is generally easier and more effective than any other method of purification for strontium nitrate and other

73

compounds whose range of solubility permits its use. On the other hand, it is often very difficult to wash out all the soluble salts from a large mass of insoluble material; and, further, two insoluble compounds, such as strontium carbonate and calcium carbonate, cannot be mechanically separated. We may expect, therefore, to find the commercial strontium carbonate of a grade available in quantity for pyrotechnic purposes to be contaminated with sodium salts, originating in the sodium carbonate used in the preparation of strontium carbonate, together with calcium carbonate as well.

The presence of calcium carbonate is due to the fact that the celestite used as the source of strontium compounds will never be entirely free from lime, and this lime will follow the strontium during the whole course of treatment, owing to the great similarity between calcium and strontium compounds.

Strontium carbonate is not as important a salt in the manufacture of pyrotechnics under present practice as is strontium nitrate, and should the time ever come when it would be required in large quantities we believe it will be found necessary to prepare it from soluble strontium salts from which the calcium compounds have been removed by a process of crystallization. Further, the utmost precaution must be taken to remove the sodium salts from the strontium carbonate, by an elaborate process of washing. One of the most difficult operations to accomplish in commercial practice is the complete separation of soluble from insoluble material, and in this case in particular the process will be found to be a difficult one, owing to the tendency of such compounds as strontium carbonate to occlude or absorb salts of alkalies.

AVAILABILITY OF SUPPLY.

This has already been dealt with under the subject of strontium nitrate. If large quantities of strontium carbonate were required, the only additional factor necessary would be to provide the factories with a more elaborate washing system than they now have. It would take but a very short time to do this, and as stated under strontium nitrate, it would be possible to produce any quantity of the material that might be desired.

USES OTHER THAN IN PYROTECHNICS.

The use of strontium carbonate in commercial practice is very limited; perhaps its most important application is in the sugar industry. By heating the strontium carbonate in a manner similar to that employed in the calcination of lime from limestone, it is converted into the oxide. When taken up with water, strontium hydrate is formed, which is used to precipitate sugar from molasses; a strontium compound is formed from which crystallized sugar may be later obtained.

PHYSICAL PROPERTIES.

Color.—Pure strontium carbonate is a white amorhpous powder. The commercial product is slightly yellow, due probably to the presence of a small amount of iron compounds. It has no odor.

Solubility.—One liter of water dissolves 0.0109 gram strontium carbonate at 24° C.

Hygroscopicity.—The substance is not hygroscopic and does not alter on exposure to the air.

Flame color.—It imparts the usual crimson color peculiar to strontium compounds to the flame.

Fusibility.—The substance is infusible, but decomposes at a high temperature into carbon dioxide and strontium oxide.

Taste.—It is tasteless.

Hardness.—As the manufactured product is in the form of a very fine amorphous powder, the hardness is not reported nor is any reference made to tenacity and opacity.

Specific gravity.—The specific gravity of the substance is 3.62.

CHEMICAL PROPERTIES.

The molecular weight of strontium carbonate is 147.635. This is made up of strontium with an atomic weight of 87.63, carbon with an atomic weight of 12.005 and three atoms of oxygen with a combined atomic weight of 48. The salt is slightly alkaline to litmus, owing to the fact that strontium carbonate is somewhat soluble in water. It is the strontium salt of carbonic acid, having the formula $SrCO_3$.

The principal reactions of strontium carbonate are those which it shares in common with the carbonates of the metals

designated as the alkaline earths, such as barium, calcium, and magnesium. Carbonic acid is a weak acid, and as these metals are relatively strong bases their carbonates retain slightly basic properties. Before the blow pipe, strontium carbonate loses carbon dioxide, strontium oxide being formed. This compound, which is very similar to quicklime, is a strong base, having the property for example of liberating ammonia from ammonium salts. When treated with any free mineral acid, such as nitric acid, the weaker carbonic acid is replaced, carbon dioxide escaping and the strontium salt of nitric acid is produced. Also, when heated with an acid anhydride such as tungstic anhydride (WO_3) or silica (SiO_2), carbon dioxide is liberated, and the salt of strontium corresponding to the anhydride used is produced. Strontium carbonate is neither an oxidizer nor a reducer under ordinary conditions.

FUNCTION IN PYROTECHNIC PIECES.

At the time when this book is written, strontium carbonate is used by but two American manufacturers, who employed it in red-signal compositions containing a mixture of four parts of strontium carbonate, twelve parts of potassium chlorate, and two parts of orange shellac. In these compositions, the potassium chlorate furnishes the oxygen to consume the shellac, thus giving the necessary heat. Under the influence of the high temperature, the strontium carbonate will break down as has been indicated, into carbon dioxide and strontium oxide.

The use of strontium carbonate is to be recommended in connection with potassium chlorate, as its basic character will permit the absorption of any free acid which may exist in the composition when made, or which may be subsequently produced, thus removing the danger of storing or handling compositions containing potassium chlorate.

QUALITATIVE TESTS.

Flame test.—This test shall be made in the ordinary manner by means of a platinum wire moistened with concentrated hydrochloric acid, dipped in the powdered salt and heated in a Bunsen burner. This test is made for the purpose of determining the purity of the salt in a very general

way in order to indicate the method of procedure. The flame produced should be a clear scarlet red.

Sulphates.—From 1 to 5 grams of the material shall be dissolved in approximately 50 c. c. of 1 : 3 hydrochloric acid and the solution boiled. After filtering, a solution of barium chloride shall be added; the formation of a white precipitate of barium sulphate indicates the presence of sulphates.

Iron compounds.—As iron compounds can be tested for and determined at the same time, this subject is discussed under "Quantitative Tests." The same statement applies to salts of calcium.

Salts of magnesium.—From 1 to 3 grams of the material shall be dissolved in hot dilute hydrochloric acid. After filtering, the solution shall be rendered slightly alkaline with ammonia, and a slight excess of ammonium carbonate and ammonium oxalate shall be added, thus precipitating the iron, strontium, and calcium compounds. Filter, and to the filtrate add a small amount of a solution of di-sodium-hydrogen phosphate; then add sufficient concentrated ammonia to the solution to make up one-third of the total volume and allow the solution to stand in a cool place for several hours. The presence of magnesium will be indicated by the formation of a white crystalline precipitate of ammonium-magnesium phosphate.

The qualitative examination of two samples of strontium carbonate gave the following results:

Flame test.—The presence of calcium and sodium salts in considerable quantity was clearly indicated, as the flame produced did not show the clear strontium red for some time, the color being obscured by the calcium and sodium compounds. Further, the presence of sulphates was shown, but compounds of magnesium were absent.

From the method of manufacture of the strontium carbonate it is evident that it may contain the following:

    Moisture.
    Insoluble matter.
    Iron compounds.
    Calcium compounds.
    Strontium sulphate.
    Sodium sulphate.
    Sodium carbonate.
    Strontium carbonate.

QUANTITATIVE TESTS.

The quantitative determinations are based on the assumption that the strontium carbonate under investigation is a reasonably pure commercial product, such as is now available.

Moisture.—A weighed sample of from 3 to 5 grams shall be spread out on a 3-inch watch glass and dried in an air bath at 130° C. to constant weight. The loss in weight thus determined divided by the weight taken will give the percentage of moisture contained in the sample.

Insoluble matter.—Five grams of the sample shall be dissolved in 100 c.c. of 1:1 hydrochloric acid. During this operation crystals of unaltered Celestite may appear. If the solution is thoroughly boiled for some time, however, this strontium sulphate will itself go into solution owing to the fact that it is quite soluble in hot hydrochloric acid of the concentration used. After the decomposition is complete, the solution shall be filtered through quantitative paper, the residue thoroughly washed with hot water, ignited and weighed. The weight obtained, divided by the weight of the sample taken, will give the percentage of insoluble matter.

Iron compounds.—To the filtrate from the insoluble matter, a slight excess of ammonia shall be added and the solution boiled for two minutes. The iron will be precipitated as ferric hydrate, $Fe(OH)_3$; the solution shall then be filtered through quantitative paper, the residue washed thoroughly with hot water, ignited and weighed as Fe_2O_3. The weight obtained divided by the weight of the sample taken will give the percentage of iron compounds which shall be reported as Fe_2O_3.

Calcium compounds.—Five-tenths gram of the sample shall be dissolved in a little nitric acid, and the solution evaporated to dryness to remove the excess of the acid used. The residue shall then be dissolved in a few drops of water, 30 c. c. of amyl alcohol shall be added, and the solution boiled until the water has all been driven off. This will be accomplished when the boiling point of the solution rises to 128° C. Under these conditions the strontium nitrate will be insoluble, with the exception of a very small amount for which

correction shall be made later on, while the calcium nitrate will all be in solution. The solution shall now be filtered through a Gooch crucible, and the volume of the filtrate noted; the residue shall be washed thoroughly with small amounts of amyl alcohol which has been previously boiled to remove any water which it might contain, and the combined filtrates evaporated to dryness. The residue shall then be dissolved in water, filtered to remove any insoluble matter, and the residue thoroughly washed with hot water. A few drops of ammonia and ammonium chloride shall then be added to the filtrate, and the calcium precipitated therefrom by the addition of a large excess of ammonium oxalate to the boiling solution. The solution shall be kept in a warm place for two hours and then filtered and the precipitate washed thoroughly with hot water, until the excess of ammonium oxalate is entirely removed. The filter paper shall then be removed from the funnel, opened up, and spread out on the side of a 400 c. c. beaker; 200 c. c. of 1:20 sulphuric acid shall then be added and the solution titrated with potassium permanganate, of approximately one-tenth-normal strength. The oxidation of the calcium oxalate in the presence of sulphuric acid takes place according to the reaction:

$$5CaC_2O_4 + 2KMnO_4 + 8H_2SO_4 =$$
$$5CaSO_4 + 10CO_2 + K_2SO_4 + 8H_2O + 2MnSO_4$$
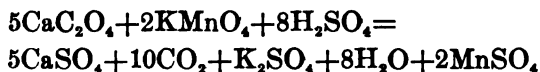
$2KMnO_4$ is equivalent to 5 atoms of available oxygen under acid conditions, its oxidizing power being represented by the equation:

$$2KMnO_4 + 3H_2SO_4 = 5O + K_2SO_4 + 2MnSO_4 + 3H_2O.$$
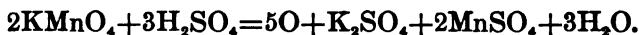
It is evident that 1 atom of available oxygen represents 1 molecule of CaC_2O_4, or 1 atom of available oxygen is equivalent to 1 molecule of CaO. Now CaO has the molecular weight 56.07 and oxygen has the atomic weight of 16, consequently 56.07 divided by 16 will give the factor necessary to multiply the weight of available oxygen consumed by the calcium oxalate, as determined by the titration, in order to derive the CaO content of the calcium oxalate titrated. This factor is 3.504.

In Gooch, "Methods in Chemical Analysis" on page 167, the solubility of strontium nitrate in amyl alcohol is stated to be 0.0008 gram for 10 c. c. It is further stated that the amyl alcohol used for washing the strontium nitrate in the method outlined above will not dissolve any of the strontium nitrate. Consequently the calcium oxalate as precipitated and titrated must be corrected for a strontium-oxalate content equivalent to 0.0008 gram of strontium nitrate for each 10 c. c. of the original amyl-alcohol filtrate, whose volume was above noted. The reaction which takes place between strontium oxalate and potassium permanganate in acid solution is precisely similar to the reaction for the corresponding calcium compound. One molecule of strontium nitrate is equivalent to 1 molecule of strontium oxide, which in turn is equivalent to 1 atom of oxygen. Strontium nitrate has the molecular weight of 211.65, and the atomic weight of oxygen, 16, divided by this molecular weight, will give the factor by which the weight of strontium nitrate remaining in solution in the amyl alcohol must be multiplied in order to obtain the amount of available oxygen consumed during the titration by the strontium oxalate produced therefrom as above stated. This factor is 0.0756. Consequently in order to get the amount of strontium nitrate which remains in solution in the amyl alcohol, multiply the volume in c. c. of the original filtrate by 0.0008 gram; then multiply this result by the factor 0.0756. Deduct this result from the total amount of the available oxygen consumed during the titration. The difference multiplied by the factor 3.504 will give the weight of calcium compounds in the sample used, expressed in terms of calcium oxide, and this weight divided by the weight of the sample taken will give the per cent. of calcium oxide.

Insoluble sulphates ($SrSO_4$).—An examination of the water extract of the sample showing the presence of soluble sulphates, it is evident that if any insoluble sulphates are present, they should be reported as strontium sulphate. Their presence will be due to the fact that the sample contains some of the original celestite from which it was made. In order to determine the amount of strontium sulphate contained in the sample, 1 gram

of the sample, from which the soluble salts have been removed by washing with water, shall be dissolved in hot 1:1 hydrochloric acid, taking care that the boiling is continued long enough to disolve any crystalline particles which may remain after the strontium carbonate itself has gone into solution. The solution shall then be filtered, made up to a volume of 400 c. c., and the hydrochloric acid neutralized with ammonia, using a solution of methyl orange for an indicator. When the neutral point has been reached, 2 c. c. of concentrated hydrochloric acid shall be added, the solution heated to boiling and the sulphates precipitated as barium sulphate by the addition of a hot 10 per cent. solution of barium chloride in slight excess. As the amount of strontium sulphate present is always small, it is necessary to allow the solution to stand for at least six hours before filtering. After standing, the solution shall be filtered through ashless paper, and the precipitate washed with hot water until the washings will give no test for chlorides with silver nitrate. The precipitate shall then be ignited and weighed as $BaSO_4$.

One molecule of barium sulphate is equivalent to 1 molecule of strontium sulphate. As barium sulphate has the molecular weight 233.43 and strontium sulphate the molecular weight 183.69, it is evident that the weight of barium sulphate obtained multiplied by the fraction $\frac{183.69}{233.43}$ or 0.787, will give the weight of strontium sulphate in the sample. This weight of strontium sulphate divided by the weight of the sample taken will give the percentage of the strontium-sulphate content.

Soluble sulphates (sodium sulphate), sodium carbonate, and total sodium salts.—Five grams of the sample shall be weighed out and thoroughly extracted and washed with hot water. The filtrate shall be evaporated to dryness, taken up with a little water, and filtered to remove the small amount of strontium carbonate which the large volume of water used in making the extraction has carried into solution. The sodium carbonate in the filtrate shall be titrated with dilute hydrochloric acid of known strength, using methyl orange for an indicator. Two molecules of hydrochloric acid of a total molecular weight of 72.936 are equivalent to 1 molecule of sodium carbonate having the molecular weight of 106.005, consequently the weight of hydro-

chloric acid used, multiplied by $\frac{106.005}{72.938}$ or 1.453 will give the weight of the sodium carbonate content, and this weight divided by the weight of the sample taken will give the percentage of sodium carbonate.

After titrating with the hydrochloric acid, two drops of sulphuric acid shall be added to the solution which shall then be evaporated to dryness in a weighed platinum dish. The residue shall be heated to remove the excess of sulphuric acid and to oxidize traces of organic matter. The total sodium salts contained in the sample are now in the form of sodium sulphate and they shall be weighed as such. The weight of sodium sulphate thus obtained must be corrected for the sodium carbonate content as determined by the titration.

As 1 molecule of sodium carbonate having the molecular weight of 106.005 is equivalent to 1 molecule of sodium sulphate having the molecular weight of 142.06, the weight of sodium carbonate as determined by the titration multiplied by $\frac{142.06}{106.005}$ or 1.34 will give the amount of sodium sulphate produced by the sodium carbonate in the sample. This weight of sodium sulphate deducted from the sodium sulphate obtained will give the weight of sodium sulphate that is present as such, and this weight divided by the weight of the sample taken will give the percentage of sodium sulphate.

As it has been the practice in this work to report all sodium compounds in terms of the equivalent weight of sodium oxide, and as 1 molecule of sodium sulphate having the molecular weight 142.06, is equivalent to 1 molecule of sodium oxide, having the molecular weight 62, it is evident that the sodium-oxide content of the sample may be obtained by multiplying the total weight of sodium sulphate obtained above by $\frac{62}{142.06}$ or 0.4364, and this weight divided by the weight of the sample taken will give the per cent. of sodium oxide.

Strontium carbonate.—Two-tenths gram of the sample shall be weighed out and thoroughly extracted with successive small amounts of hot water. The volume of the water should be kept as small as possible in order to avoid the error which will be caused by the solubility of strontium carbonate. After the soluble salts have been removed, the filter paper shall be taken from the funnel, opened, and laid against the side of a beaker. An excess of standard dilute hydrochloric

acid shall now be added, and the solution warmed until all the carbonates have been decomposed. Methyl orange shall now be added for an indicator, and the excess of hydrochloric acid titrated with a solution of caustic soda which has been standardized against the solution of hydrochloric acid used.

The amount of hydrochloric acid necessary to combine with the strontium carbonate and with the calcium carbonate equivalent to the amount of calcium oxide found, is thus determined. The amount of calcium oxide in the weighed sample taken shall be computed. One molecule of calcium oxide having the molecular weight 56.07 is equivalent to two molecules of hydrochloric acid, having a total molecular weight of 72.936, consequently the weight of calcium oxide in the weighted sample multiplied by the fraction $\frac{72.936}{56.07}$ or 1.301 will give the amount of hydrochloric acid necessary to combine with the calcium oxide in the weighed sample. This amount of hydrochloric acid shall be deducted from the total weight of hydrochloric acid used, the difference being the amount of hydrochloric acid necessary to combine with the strontium carbonate in the sample. One molecule of strontium carbonate having the molecular weight 147.635 is equivalent to two molecules of hydrochloric acid having the combined molecular weight of 72.936, consequently the weight of hydrochloric acid necessary to combine with the strontium carbonate as above determined multiplied by the fraction $\frac{147.635}{72.936}$ or 2.024 will give the weight of strontium carbonate in the sample, and this weight divided by the weight of the sample taken will give the percentage of strontium carbonate.

ANALYTICAL RESULTS.

In the following example, the results of the analysis of two samples of commercial strontium carbonate are given; one of these samples hereafter known as No. 1 was labeled " Commercially pure," the other known as No. 2 was labeled " Chemically pure."

Moisture No. 1:

	Grams.
Weight taken _____	3
Weight after drying_____	2.9861
Loss in weight_____	.0139

This equals 0.46 per cent.

Moisture No. 2:

	Grams.
Weight taken	3
Weight after drying	2.9909
Loss in weight	.0091

This equals 0.3 per cent.

Insoluble matter No. 1:

	Grams.
Weight taken	5
Weight insoluble matter	.0055

Equals 0.11 per cent.

Insoluble matter No. 2:

	Grams.
Weight taken	5
Weight insoluble matter	.0105

Equals 0.21 per cent.

Iron compounds No. 1:

	Grams.
Weight sample taken	5
Weight Fe_2O_3 obtained	.0135

Equals 0.27 per cent. Fe_2O_3.

Iron compounds No. 2:

	Grams.
Weight taken	5
Weight Fe_2O_3	.0025

Equals 0.05 per cent.

Calcium compounds No. 1:

	Grams.
Weight taken	0.5

2.9 c. c. $KMnO_4$ solution containing 0.0008 gram available oxygen per cubic centimeter used to titrate the calcium oxalate plus strontium oxalate obtained.

Total available oxygen consumed, 0.00232 gram.

Volume original amyl-alcohol filtrate, 20 c. c., containing 0.0016 gram strontium nitrate.

This multiplied by 0.0756 gives 0.00012 gram as the available oxygen consumed by the strontium oxalate. Available oxygen consumed by calcium oxalate equals 0.0022 gram, which, multiplied by the factor 3.504, is equal to 0.0077 gram CaO, which equals 1.54 per cent.

Calcium compounds No. 2:

                                                              Grams.
.Weight taken_____ 0.5

Solution permanganate used, 4.2 c. c.; 1 c. c. permanganate equals 0.0008 gram available oxygen; total oxygen consumed, 0.00336 gram.

Volume original amyl-alcohol filtrate 20 c. c., the correction for the strontium-oxalate content being 0.00012 gram oxygen as in No. 1. Oxygen consumed by calcium oxalate equals 0.00324 gram; this multiplied by the factor 3.504 gives 0.01135 gram calcium oxide which equals 2.27 per cent.

· *Insoluble sulphate No. 1:*

                                                              Grams.
Weight taken ____ _____5
Weight barium sulphate obtained _____ .0574

Multiplied by the factor 0.787 equals 0.0452 gram $SrSO_4$; equals 0.9 per cent. $SrSO_4$.

Insoluble sulphate No. 2:

                                                              Grams.
Weight taken _____ _____5
Weight barium sulphate obtained _____ .0279

Multiplied by the factor 0.787 equals 0.022 gram $SrSO_4$; equals 0.44 per cent. $SrSO_4$.

Sodium carbonate No. 1:

                                                              Grams.
Weight taken_____ 5
HCl used contained (acid per c. c.)_____ .00389

The volume required to neutralize sodium carbonate equals 0.6 c. c. HCl; equals 0.00233 gram HCl. Multiplied by the factor 1.453 equals 0.0034 gram Na_2CO_3; equals 0.07 per cent.

Sodium carbonate No. 2:

                                                              Grams.
Weight taken _____ _____5

Two-tenths c. c. hydrochloric acid required for sodium carbonate equals 0.0008 gram HCl; equals 0.0011 gram Na_2CO_3; equals 0.02 per cent.

Total sodium salts No. 1:

                                                              Grams.
Weight taken _____ _____5
Weight Na_2SO_4 obtained _____ .0501

Multiplied by the factor 0.4364 equals 0.0219 gram Na_2O; equals 0.44 per cent. Na_2O.

Total sodium salts No. 2:

	Grams.
Weight taken _____ _____	5
Weight Na_2SO_4 obtained _____	.0799

Multiplied by the factor 0.4364 equals 0.039 gram Na_2O; equals 0.70 per cent.

Strontium carbonate No. 1:

	Gram.
Weight taken _____	0.2
Strength standard hydrochloric acid used (per c. c.)_	.00389

One cubic centimeter NaOH used to titrate excess hydrochloric acid used is equivalent to 1.91 c. c. HCl.

	C. c.
Volume HCl used_____	35.5
Volume NaOH used for excess acid_____	5.35
HCl equivalent to NaOH used_____	10.2

HCl required for strontium carbonate plus calcium carbonate, 25.3 c. c. equals 0.0984 gram HCl.

Calcium carbonate contained is equivalent to 1.54 per cent. calcium oxide, and equals 0.0031 gram CaO in the weight taken; multiplied by the factor 1.301 equals 0.0040 gram HCl consumed by calcium compounds.

Therefore HCl required for strontium carbonate equals 0.0944 gram, multiplied by the factor 2.024; equals 0.19106 gram $SrCO_3$; equals 95.53 per cent.

Strontium carbonate No. 2:

	Gram.
Weight taken _____	0.2
	C. c.
Volume HCl used_____	35.9
Volume NaOH used for excess acid_____	5.4
HCl equivalent to NaOH used_____	10.3

Which is equivalent to 10.3 c. c. HCl. Therefore HCl used for $SrCO_3$ plus $CaCO_3$ equals 25.6 c. c., which equals 0.0996 gram HCl.

This sample contained 2.27 per cent. calcium carbonate figured as CaO. Weight CaO in sample 0.0045 gram; multiplied by the factor 1.301 equals 0.0059 gram HCl.

Therefore HCl consumed by $SrCO_3$ equals 0.0937 gram; multiplied by the factor 2.024, equals 0.18965 gram $SrCO_3$; equals 94.82 per cent.

DISCUSSION OF RESULTS.

These results indicate clearly that the samples of strontium carbonate examined still contain material amounts of substances used in their preparation. As the amount of sodium carbonate found was very small, practically all the sodium salts present may be assumed to be sodium sulphate, and the presence of this sodium sulphate is a clear indication that the samples were not thoroughly washed during their process of manufacture. Further, the presence of strontium sulphate shows that the conversion of the celestite into strontium carbonate was not entirely complete, as might have been expected from the law of mass action.

Unless a celestite can be obtained which is free from compounds of calcium, these are sure to be contained in the finished product, and it will be necessary for the manufacturer of strontium carbonate to be used for pyrotechnic purposes either to get a celestite that is free from calcium compounds, or to make the strontium carbonate from a solution of a strontium salt which has been freed from calcium compounds. The two samples of strontium carbonate examined were both very undesirable from the standpoint of the flame color which they produced, and it would be necessary to employ a purer article in order to obtain a satisfactory result. The small percentage of strontium sulphate will of course have no deleterious effect, the calcium and sodium compounds being the only harmful impurities.

SPECIFICATIONS.

In connection with the investigation made on strontium carbonate, the following specifications should be adopted for the material to be used in military pyrotechnics:

1. Material shall be white or at least show only a slight yellowish tinge.
2. The material shall be odorless.
3. When compounded the material shall be in such a state of division that all will pass through a 100-mesh sieve.
4. The material shall contain not less than 99 per cent. of strontium carbonate.

5. The material shall contain not more than 0.2 per cent. moisture when compounded.
6. The material shall contain not more than 0.5 per cent. of calcium or magnesium compounds, or of both together, calculated as their oxides.
7. The material shall not contain more than 0.5 per cent. of iron compounds calculated as Fe_2O_3.
8. The material shall not contain more than 0.25 per cent. of sodium salts, calculated as sodium oxide.

DISCUSSION OF SPECIFICATIONS.

No new points occur in these specifications as regards the impurities present and their effect which have not already been covered in the chapter on strontium nitrate. Attention is called to the fact that the samples do not meet the requirements above set forth.

CHAPTER VII.

ARSENIC.

HISTORY.

Arsenic has been known since the earliest times, not in the form of the metal, to be sure, but as various compounds, particularly as the sulphides. The word comes from a Greek root, meaning " masculine or strong," which doubtless had reference to its poisonous properties.

Aristotle gave the sulphides of arsenic the name sandarake, and Theophrastus mentions them under the name of harsenikon. Arsenic, however, seems to have been known to some of the Greek alchemists, who obtained it as a sublimate which was capable of turning copper white, and was, therefore, regarded by them as a variety of mercury. The white oxide is mentioned by the Greek alchemist, Olympiodorus, who made it by roasting arsenic sulphide. He gave it the name of white alum. All these substances were known to the later alchemists, who used them to give a white color to copper in their attempts to transmute copper into silver.

Abertus Magnus was the first to note that these compounds contained a substance resembling a metal, but other alchemists regarded it as a bastard or semi-metal and called it arsenicum rex.

In 1773 G. Brandt showed that white arsenic was the calx of the element, and after the downfall of the Phlogistic theory it was regarded correctly as the oxide of the element.

OCCURRENCE IN NATURE.

Arsenic in small quantities is one of the most widely distributed elements; it is found in mineral and other waters, in coal smoke, in most pyritic minerals, and in a large number of ores.

In England it occurs principally with tin ore, and on the Continent in mispickel. Arsenic occurs native (usually asso-

ciated with iron, cobalt, nickel, antimony, and silver) in crystalline rocks and in the older schists, generally in reniform and stalactitic masses, often lamellated; it also occurs occasionally in rhombohedral crystals. At Zmeov, in Siberia, large masses are found; it occurs in the silver mines of Freiberg, Annaberg, Marienberg, and Schneeberg, in Saxony; at Joachimsthal, in Bohemia; Andreasberg, in the Hartz; Kapnik, in Transylvania; Orawitza, Hungary; St. Maria-aux-Mines, in Alsace; in Borneo; and in the United States.

Arsenic disulphide, which is used in pyrotechnics, is an artificially prepared product in the United States. It may be obtained, however, by grinding native realgar or ruby sulphur, also known as rothesrauschgelb, rothes schuefel, sulphure rouge, orpin rouge, risigallo and sandaracha. As realgar, it is found in sufficiently large deposits in Saxony, Germany, and in Japan, to be available after grinding the mineral for use. The mineral As_2S_2 is composed of 70.04 per cent. of arsenic and 29.96 per cent. of sulphur when pure. It is a soft orange-red mineral, of resinous luster, usually occurring in translucent granular masses, but also compact and in transparent monoclinic crystals. The most notable deposits are in Hungary and the island of Borneo. Deposits are found in Utah, California, and Wyoming.

Another very important arsenic mineral is orpiment which has the formula As_2S_3, and is composed of 60.91 per cent. arsenic and 39.09 per cent. sulphur. It is found in lemon-yellow, foliated masses, which cleave into thin, pearly, flexible scales, and also granular masses like the yokes of hard boiled eggs. It occurs less frequently as reniform crusts and imperfect orthorhombic crystals.

Arsenolite is the native oxide of arsenic, having the formula As_2O_3, being composed of 75.75 per cent. arsenic and 24.25 per cent. oxygen. It occurs as minute white hair-line crystals, or yellowish or white crusts upon arsenical ores; very rarely as distinct octahedral crystals of a sweetish taste. As arsenide, it occurs combined with iron in two forms, $FeAs_2$ and Fe_3As_4; with nickel as kupernickel, $NiAs$ and $NiAs_2$; with cobalt, as tin-white cobalt arsenide, $CoAs_2$. With antimony it occurs as arsenical antimony, at Przibram in Bohe-

mia; with blende, antimony and spathic iron, at Allemont and Schladming in Styria and Andreasberg in the Hartz.

With oxygen, arsenic occurs as arsenolite or arsenite, with pyrites, or white mundic FeS_2, $FeAs_2$; with sulphur and cobalt in cobalt glance CoS_2CoAs_2, and in a number of other ores. It is obtained as a secondary product in the roasting of tin, copper and nickel ores, arsenical ores, smaltine, cobalt and nickel glance, etc.

Arsenolite or arsenite, As_2O_3, usually is found as a crust on other arsenical minerals, being formed by their decomposition.

The arsenite of copper, known as Scheele's green, having the formula $CuHAsO_3$, is a very well-known artificially prepared substance. It is formed on mixing together an aqueous solution of potassium arsenite with a solution of sulphate of copper when a brilliant green precipitate is thrown down.

TOXICOLOGY.

Since the very earliest times the poisonous properties of arsenic compounds have been known and their use as poisons has been common. The noted poisoners of history, such as the Borgia family, used it frequently, and the records of the courts of criminal practice to-day include many cases in which poisons containing arsenic in some form play an important part.

Almost all the compounds of arsenic are poisonous in their nature, although the metal itself and the disulphide are not supposed to be directly poisonous in themselves. At the same time, the ease with which they form other compounds, which are poisonous, will render any exposure to them extremely dangerous. Poisoning by arsenic may result from the gradual absorption of its compounds, or from a succession of small doses as by its inhalation in the form of a dust, or by its gradual absorption by the body, which takes place, for example, when the walls of living rooms are covered with paper colored with arsenic compounds as was the common practice a few decades ago. However the arsenic is acquired, it seems to affect the same set of organs, resulting in symptoms resembling gastritis.

In the year 1900 the hospitals of Manchester, England, were filled with patients suffering from arsenical poisoning. This was soon traced to the beer which they had been using, which was manufactured from glucose, in producing which sulphuric acid containing arsenic was used. Several thousand cases developed and the mortality was great.

Arsenical poisoning is developed in many industrial operations, the materials being so poisonous that small amounts only are required to produce the effect. People handling the material fail to realize the danger they are in, particularly as every portion of the body which is exposed to arsenical materials in the form of dust or otherwise will absorb these materials to a dangerous and often fatal extent.

Arsine, the hydride of arsenic AsH_3, which is a gas, is probably the most poisonous of the compounds of this element. Its discoverer was killed by inhaling one bubble as it passed through water. We cannot emphasize too strongly the danger in handling all arsenical materials, particularly as it is difficult to impress those unacquainted with the subject with the importance of the extreme precautions necessary for safety.

A detail of men, working in the various pyrotechnic plants which were in operation in October, 1918, were required to mix the smoke-tracer composition, and to place the mixture thus compounded in the smoke-tracer containers elsewhere described. This smoke-tracer composition contained disulphide of arsenic, part of which consisted of ground realgar, a native mineral free from the poisonous oxide of arsenic. Owing to the scarcity of realgar a manufactured product was used in part, which later proved to have a large content of the poisonous oxide. Within a week the men working with this poisonous material developed sores on their hands and faces to such an extent that they were no longer able to perform their duties. Had they been allowed to continue, the results might have been disastrous.

Another instance of fatal arsenical poisoning, developed during an industrial process, is in connection with the cyanide process now so generally used in the treatment of low-grade gold ores in the gold-mining regions of the world. During this process the gold, after having been dissolved in a solution of cyanide of potassium or sodium, is precipitated

from the solution on thin zinc shavings. If the ores contain any arsenic, some of it will be deposited along with the gold on the zinc. The next step of the operation consists in dissolving the excess of zinc with sulphuric acid, resulting in the liberation of the arsenic in the form of the gas arsine. Fatal cases of poisoning are on record, caused by the inhalation of the mixture of arsine and hydrogen which is produced by the action of the sulphuric acid on the zinc. Any commercial operation which has to do with substances containing any arsenic whatever is to be regarded as in a dangerous class, and the utmost precaution must be taken to protect all those engaged therein.

METHOD OF MANUFACTURE.

Arsenic disulphide is prepared by fusing together arsenious oxide (As_2O_3) and sulphur or orpiment (As_2S_3) in the proper proportions. On the large scale it is obtained by the distillation of a mixture of arsenical ores, such as arsenic and iron pyrites with sulphur or sulphide of arsenic, which has been precipitated in the purification of sulphuric acid. In this operation about 15 per cent. of arsenic and from 26 to 28 per cent. of sulphur are mixed and placed in a flask-shaped earthenware retort which has capacity for a charge of 60 pounds when two-thirds full. The receivers are made to hold approximately the same amount of material. The retort is gradually heated to redness and so kept for a period of 8 to 12 hours. Crude realgar is formed under these conditions, and is compact, dark and rich in arsenic; if sulphur is in excess, the material is friable and light red. The crude realgar is remelted rapidly with the requisite amount of sulphur, or with realgar of a poor quality, and poured into cast-iron containers. The mass is cleared of slag and heated until quite fluid and until a small quantity shows the proper appearance on cooling. It is then poured into conical sheet-iron molds. It is ground and then ready for use. Greater care must be employed in the preparation of realgar than in the manufacture of orpiment, and an assay must be frequently made to ascertain the exact proportions required before the final melting.

The arsenious oxide which is used in the preparation of realgar or arsenic disulphide is made by roasting arsenical ores, such as mispickle, in a reverberatory furnace. The products of this roasting are carried into vapor chambers having large condensing surfaces. The arsenical deposit from these vapor chambers is refined by sublimation by admitting it into another reverberatory furnace shorter in length than that used in the roasting of the ores. The charge is admitted from the top and padded down through doors at the side, more being added as the materials sublime. The sublimates are caught in vapor chambers having larger condensing surfaces than those used in the roasting of the ores. The fuel used is smokeless and is made of anthracite and coke mixed together. The resublimed product is then ground between millstones and fed into kegs from a hopper through a leathern hose which fastens to the top of the cask and prevents any escape of the powder.

AVAILABILITY OF SUPPLY.

There are large deposits of arsenical ores in the United States. There is also reported a large quantity of low-grade realgar in the State of Washington. There are numerous deposits in Hungary, Germany, and Japan. The following table from the Mineral Industry of 1917 gives the production and importation figures for arsenious oxide and arsenic sulphide.

IMPORTS.

The imports of arsenic in 1917 given by the Department of Commerce, as " Arsenic of arsenious acid," were 1,178 tons, valued at $264,534, compared with 1,071 tons, valued at $107,876, in 1916. The increase is due to the resumption, after a lapse of more than a year, of imports from Mexico in June. The imports from Canada in 1917 were about the same as in 1916. Comparatively little arsenic came from other foreign countries.

Statistics of arsenic in the United States.[1]

[Short tons.]

| Year. | White arsenic. | | | | | | | Sulphide of arsenic—Imports. | | |
| | Production. | | Imports. | | Supply. | | | | | |
	Tons.	Value.	Tons.	Value.	Tons.	Value.	Per ton.	Tons.	Value.	Per ton.
1903...	611	$36,691	606	$38,505	1,217	$75,196	$61.79	3,523	$256,097	$72.70
1904...	36	2,185	204	16,899	2:0	19,084	79.50	3,196	226,481	70.87
1905...	754	35,210	616	37,342	1,370	72,552	52.96	3,222	219,198	68.03
1906...	737	63,460	167	13,436	904	76,896	85.07	3,820	336,609	88.12
1907...	1,751	168,000	203	21,558	1,954	184,558	94.47	4,961	553,440	88.61
1908...	1,302	99,193	168	13,263	1,470	112,456	76.46	4,796	417,137	86.97
1909...	1,214	52,946	444	31,235	1,638	84,181	51.39	3,592	272,493	75.86
1910...	1,497	52,305	1,010	62,590	2,507	114,895	45.83	4,128	251,716	60.97
1911...	3,132	73,408	1,921	116,948	5,053	190,356	37.68	2,702	159,626	59.04
1912...	3,141	190,757	3,103	200,616	6,244	391,373	62.68	3,379	246,815	73.04
1913...	2,513	159,236	1,519	133,597	4,032	292,833	72.62	3,344	285,537	85.38
1914...	4,670	313,147	1,594	109,121	6,244	422,268	67.42	2,040	165,266	81.03
1915...	5,498	302,116	1,400	113,677	6,898	415,793	60.28	1,787	154,517	86.46
1916...	5,986	555,187	1,071	107,876	7,057	663,063	93.96	1,090	124,844	114.49
1917...	6,151	1,118,313	1,178	264,534	7,329	1,382,847	188.08	2,776	410,341	147.80

[1] Production from the United States Geological Survey; imports from Department of Commerce.

World's production of arsenic (in metric tons).

Year.	Canada.[1]	Germany.[2]	Italy.[2]	Japan.[1]	Portugal.[2]	Spain.[2]	United Kingdom.[1]	United States.[1]	France.[2]
1902............	726	2,828	....	12	736	71	2,165	1,226	5,372
1903............	233	2,768	50	6	698	1,088	916	554	658
1904............	66	2,829	80	4	1,370	400	992	452	3,117
1905............	Nil.	2,535	....	8	1,562	1,140	1,552	701	3,627
1906............	Nil.	3,052	....	5	1,322	1,114	1,625	754	6,534
1907............	317	2,904	73	7	1,538	2,400	1,523	916	7,900
1908............	649	2,822	451	20	1,655	2,004	2,007	1,301	2,381
1909............	1,020	2,911	Nil.	8	1,420	506	2,911	914	2,141
1910............	1,363	3,066	Nil.	12	974	444	2,187	1,203	8,045
1911............	1,815	2,981	16	6	887	331	2,178	2,800	19,000
1912............	1,858	4,869	Nil.	....	1,006	(4)	2,228	2,855	81,880
1913............	1,538	5,008	Nil.	....	925	....	1,716	2,158	70,613
1914............	1,576	....	Nil.	....	960	....	2,007	4,338	....
1915............	2,174	....	Nil.	15	....	....	2,536	4,990	....
1916............	1,983	....	Nil.	(4)	....	....	2,575	5,430	....
1917............	(4)	....	(4)	(4)	....	....	2,616	5,285	....

[1] White arsenic. [2] Oxide, sulphide, etc. [3] Ore. [4] Not yet available.

USES OTHER THAN IN PYROTECHNICS.

Arsenic is used in certain alloys, in the bronzing of brass, and the manufacture of opal glass. Arsenious oxide is a powerful febrifuge, being sometimes efficacious when quinine has failed. It is used in glass making to remove the color which is produced by the lower oxide of iron. It is used in enameling, calico printing, and when mixed with about 20 per cent. of its weight of sodium carbonate it is used to prevent boiler incrustation. It is also used for fly and rat poison and as a constituent of sheep dip and in certain forms of insecticides. For the last purpose, the compounds generally used are the arsenates of lead and calcium, and such other compounds as Paris green and London purple. It is used in the holds of ships as a preservative to prevent vegetable growths; it is found as a pigment in various colors, such as green, blue, pink, white, brown, etc. In India it is used as wash for walls to prevent insect ravages. Arsenical soaps are used in preserving the skin. It has distinct commercial value in the fixation of aniline colors, especially aniline blue. Its use is principally for perfecting steam colors, either as a solution in glycerol, containing 4 pounds of oxide to 1 gallon of glycerol under the name of " Arsenic and glycerine standard," or as sodium arsenite in sodium carbonate or borate. In medicine we find it used as Fowler's solution, which contain 4 grains of arsenious acid in the form of sodium arsenite in each ounce of fluid. It is used in India as a specific antidote for hydrophobia and serpent poisoning. In veterinary medicine it is used as a tonic and to eradicate worms and for improving the coats of horses. A hydrated sodium arsenite is used as a substitute for animal dung in dyeing. The arsenite of chromium and iron is used as a green pigment.

Schweinfurth green has the formula $3CuO,As_2O_3.-Cu(C_2H_3O_2)_2$ and is known as aceto-arsenite of copper. The arsenate of sodium, having a formula Na_2HAsO_4 is also largely used in calico printing as a substitute for animal dung. Realgar and orpiment are used as pigments. Arsenious chloride and iodide are used to a slight extent in medicine. Cacodylic acid, having a formula $(CH_3)_2 AsO. OH$, is used in medicine. Disodium methylarsenate (arrhenal)

$CH_2AsO(ONa)_2$ is used as a treatment for the sleeping sickness. Tolyl arsenic acid $CH_3C_6H_4AsO(OH)_2$ is efficacious in destroying trypanosomes. Other arsenic drugs of interest are sodium acetyl-p-aminophenylarsenate $CH_3CONHC_6H_4$-$AsO(OH)ONa$ and arsenophenyglycine $As_2(C_6H_4NHCH_2$-$CO_2H)_2$. Arsenogene is an indefinite compound of peptonized casein and arsenic of distinct medicinal value.

Generally speaking, the medical action of arsenic in small doses is as a tonic, the effect being the same howsoever the material is introduced into the system. It is a gastric stimulant and promotes the formation of red corpuscles and increases their haemoglobin content. It has some power not yet understood of effecting general metabolism, and profound changes are often produced by the use of the drug. It is also used as an alterative. It is eliminated chiefly by the kidneys and is stored principally in the liver and kidneys. It is used generally in the treatment of debilitating diseases and in the form of certain complex organic derivaties, such as the sodium salt of cacodylic acid; it is a specific for pernicious blood diseases of an inherited or acquired nature.

In certain localities where arsenic is common, such as in Styria, the natives acquire the habit of eating arsenic, under the name of "Hydrach" to increase their endurance. They begin with small doses which are gradually increased until the amount which they can take is several times the fatal dose for a person who is not accustomed to it. They increase in strength and weight, and their complexions become very clear. It is said that they live long but die suddenly, and instances are known where the habit existed over 40 years. Instances are known in the western part of the United States, where prospectors attracted by a spring of sweet water have located their cabins near by, the sweetness of the water being due to arsenic. With men the results were disastrous, whereas cattle and horses, having access to similar springs, became fat and sleek and apparently in the best of condition.

PHYSICAL AND CHEMICAL PROPERTIES OF ARSENIC DISULPHIDE.

In realgar derived from the native mineral, it is evident that the substances which may be contained as impurities will be principally the gangue of the rock in which the mineral occurs. This gangue may vary in its composition within wide limits. Also, the percentage of realgar present will be found to vary, one sample with another. Specimens of material which were imported from Saxony before the war showed, after the arsenic disulphide was dissolved, that the residue consisted principally of particles of silica and red crystalline particles of a mineral probably belonging to the garnet family. An examination of similar material from Japan showed that it was a remarkably pure specimen, the percentage of silica and other foreign material being but small.

Attention was first directed to the manufactured product of American origin by reports that those men working with it had sores on their hands and faces. The soreness of the hands and faces developed only when the manufactured American product was used, the imported material, which was the crushed native mineral, gave them no trouble. The war conditions, however, had cut off the Saxony supply, and the amount obtainable from Japan was small and uncertain, consequently it was necessary to fall back on the American product, which seemed to be so poisonous to the operators that they anticipated difficulty in being able to work with the material. An examination of samples of the American and foreign material showed that the Japanese and Saxony product was very much darker in color than the American, and this suggested the probability that the American material was possibly contaminated with the poisonous oxide of arsenic.

Arsenic disulphide is not soluble in hydrochloric acid, while the poisonous oxide, As_2O_3, is soluble, consequently a sample of the American product which was giving the trouble was boiled with 1:1 hydrochloric acid, in order to dissolve out any poisonous oxide which might be present. It was noticed that the extraction with the acid darkened the color of the sample very materially, until it acquired the

same dark-orange color as the imported product. The examination of the filtrate from this extraction showed the presence of large amounts of arsenic in solution, the quantitative amounts being given under the heading "Analytical results." This sample contained 44 per cent. of the poisonous oxide in a state of fine division, and the troubles which the manufacturers were having in the use of the material were thus explained. The wonder is that they were not more serious in their nature. On the other hand, the Saxony and Japanese materials, on being thoroughly extracted with hydrochloric acid, showed practically no trace of the poisonous oxide, and, as arsenic disulphide itself is not poisonous, no difficulty was experienced by the workmen. A further examination of the American product showed that it contained 24.78 per cent. of total sulphur. As the sample contained 44 per cent. of As_2O_3, the possible sulphur content could be but 16.75 per cent., consequently the sample must contain free sulphur. In order to determine this, a weighed amount was extracted with carbon bisulphide, followed by hot absolute alcohol. The extract on evaporation showed the presence of a large amount of sulphur, and the sample suffered a corresponding loss in weight. The quantitative results are given a little later on.

Further, the examination of the hydrochloric-acid extract, after precipitating the soluble arsenic therefrom, showed the presence of a small amount of iron. These results indicate the determinations which should be made in the chemical examination of arsenic disulphide for use in pyrotechnic purposes.

The disulphide of arsenic volatilizes easily before the blowpipe, giving off the characteristic garlic odor together with that of burning sulphur. It is insoluble in water or hydrochloric acid. It occurs in nature as the mineral realgar which is found in monoclinic crystals of a specific gravity of 3.4 to 3.6 and a hardness of 1.5 to 2. It has a resinous luster and orange-red streak. It is found transparent or translucent and in tenacity is slightly sectile. Its color is red, which becomes orange on exposure. The manufactured product is fusible at a low temperature, forming a solid mass which is heavy, friable, and easily powdered. Workmen who have become accustomed to making the material can judge,

of its quality by its color and brittleness. The substance is not hygroscopic, and is not affected by exposure to the air. It does not impart color to the flame.

ANALYTICAL METHODS.

The following methods of analysis are based on the assumption that the material examined is the ordinary product of the usual commercial grade of purity. It may be either a manufactured article or one made by grinding the native realgar.

Moisture.—Three grams of the sample shall be spread out on a 3-inch watch glass and dried to constant weight at 105° C. The loss in weight, divided by the weight of the sample taken, gives the percentage of moisture contained.

Determination of the oxide of arsenic (As_2O_3).—One gram of the finely ground sample shall be gently boiled with 100 c. c. of 1:1 hydrochloric acid for one hour. After filtering and washing, the soluble arsenic in the filtrate shall be precipitated as As_2S_3 by a current of sulphureted hydrogen. When the precipitation is completed, the excess of sulphureted hydrogen shall be removed from the solution by a rapid stream of carbon dioxide; the solution shall then be filtered through a weighed Gooch crucible, and the residue washed and dried at 105° C. and weighed as As_2S_3. This weight multiplied by the factor 0.8042 gives the equivalent weight of As_2O_3 in the sample, and this weight divided by the weight taken, gives the percentage of As_2O_3.

Free sulphur.—One gram of the finely ground material which has been weighed out in a Gooch crucible shall be repeatedly extracted with small amounts of carbon bisulphide, followed by hot absolute alcohol, which for the sake of convenience is heated in a small wash bottle. The crucible is then dried in an air bath at 105° C. The loss in weight represents the free-sulphur content of the sample, and when divided by the weight of the sample taken, the percentage of the free-sulphur content is obtained.

Total sulphur.—Five-tenths gram of the finely ground sample shall be placed in a covered No. 2 beaker, with a mixture of 1 c. c. of water, 9 c. c. of glacial acetic acid, and 6 c. c.

of liquid bromine, at room temperature and allowed to stand over night. In the morning 20 c. c. of concentrated hydrochloric acid shall be added, and the solution warmed gently for half an hour. The cover shall then be removed, and the solution evaporated near to dryness on a steam bath. The mass shall then be taken up with hydrochloric acid and diluted to 150 c. c. with hot water. To the warm solution, 0.5 gram of powdered aluminum shall be added, a little at a time to prevent foaming, until the arsenic shall have been precipitated as the metal. This operation should be done with care, under a hood preferably, to avoid any danger to the operator from the inhalation of arsine. The solution shall then be filtered and the precipitate washed with hot water. The filtrate shall be diluted to 400 c. c. and boiled. The sulphur shall then be precipitated as barium sulphate by the addition of 25 c. c. of a boiling 10 per cent. solution of barium chloride. The precipitate is allowed to stand for 10 or 12 minutes until it settles, and shall then be filtered hot. The precipitate is washed with hot water until the filtrate shows no precipitate with a solution of silver nitrate. The precipitate and filler paper are transferred to a weighed crucible' and ignited. The weight of barium sulphate obtained multiplied by the factor 0.13734 gives the sulphur content, which divided by the weight taken gives the percentage of total sulphur in the sample.

Iron.—The filtrate from the As_2S_3 precipitate mentioned above shall be thoroughly boiled to remove any traces of sulphureted hydrogen which it may still contain. A few drops of nitric acid shall then be added, and the iron precipitated as ferric hydrate by the addition of ammonia in slight excess, the solution shall then be boiled for two minutes, filtered through ashless paper, the precipitate thoroughly washed with hot water and then ignited, and weighed as Fe_2O_3.

Calculation of results.—The free-sulphur and As_2O_3 contents shall be reported as such. From the total sulphur obtained, deduct the free sulphur, the remaining sulphur multiplied by the factor 3.338 will give the As_2S_2 content, which shall be so reported. The Fe_2O_3 obtained is very small and may appropriately be reported as metallic iron, although the form in which the iron is really present is questionable;

it may come from the abrasion of the machinery used in grinding, in which case it will exist as metallic iron.

ANALYTICAL RESULTS.

Moisture:

	Grams.
Weight taken_____	3
Weight after drying_____	2.9919
Loss in weight_____	.0081

The loss in weight divided by the weight taken gives 0.27 per cent.

Oxide of Arsenic (As_2O_3).—Two examples are given as follows:

Example No. 1:

	Gram.
Weight of sample taken_____	0.4987
Weight As_2S_3 _____	.2782

This weight multiplied by the factor 0.8042 gives 0.2197 gram as the As_2O_3 content in the sample. This divided by the weight taken gives 44.06 per cent.

Example No. 2:

	Gram.
Weight taken_____	0.5014
Weight of As_2S_3_____	.2782

This multiplied by the factor 0.8042 gives 0.2197 gram as the As_2O_3 content of the sample. This divided by the weight taken gives 43.82 per cent. The average of these two examples is 43.94 per cent.

Free sulphur.—Weight taken, 1.0011 grams. Loss in weight by carbon bisulphide and alcohol extraction, 0.1164 gram. This divided by the weight taken, gives 11.63 per cent. sulphur.

Total sulphur:

	Gram.
Weight taken_____	0.5
Weight of barium sulphate_____	.9023

This weight multiplied by the factor 0.13734 gives 0.1239 gram of sulphur. This weight divided by the weight taken gives 24.78 per cent. total sulphur.

Iron:

	Gram.
Weight taken_____	1
Weight of Fe_2O_3_____	.0027

This weight multiplied by the factor 0.7 gives 0.0019 gram metallic iron. This divided by the weight taken gives 0.19 per cent. Fe.

These results tabulate as follows:

	Per cent.
Moisture	0.27
As_2O_3 (average)	43.94
Free sulphur	11.63
As_2S_2	43.89
Iron	.19
Total	99.92

ARSENIOUS OXIDE.

Physical properties.—On account of the occurrence of As_2O_3 in the manufactured product, and the fact that it is used also as one of the substances in the manufacture of As_2S_2, a brief mention of the physical properties of the oxide may not be out of place. It exists in an amorphous or glassy form, and in two crystalline modifications. The amorphous form is transparent, becoming opaque on exposure to the air, forming the crystalline oxide. In doing this its specific gravity is diminished, and its solubility in water decreases. The vitreous variety is soluble in 108 parts of cold water, the opaque variety is soluble in 355 parts of cold water. One crystalline modification is the common form occuring in octahedral crystals; the second crystalline modification is in the form of trimetric prisms occasionally found in sublimates. By boiling the latter the former is obtained. Arsenious oxide is odorless with a sweet taste, soluble in hydrochloric acid and slightly soluble in cold water. It has a specific gravity of 3.7 and a hardness of 1.5. It is brittle and easily powdered, and gives a white streak on porcelain. It is slightly soluble in alcohol and ether, but almost insoluble in carbon bisulphide. It sublimes at 200° C. without fusion. Under pressure, however, it may be fused. The vapor is colorless and odorless. A solution of arsenious acid in water is acid to test papers, but the aqueous solution does not contain the hydrate, arsenious acid, H_3AsO_3, as might be expected.

The substance is not hygroscopic, and is not affected by exposure to the air. It does not impart color to the flame.

Chemical properties.—This oxide has the formula As_2O_3, its molecular weight being 197.92 Arsenious oxide, commonly known as white arsenic, is the anhydride of arsenious acid, H_3AsO_3. Its characteristic reactions are those of an acid and a reducer. Thus it forms salts of arsenious acid with the stronger bases, and is oxidized to arsenic acid by strong oxidizers. It is reduced to metallic arsenic or to its hydride by the stronger reducers, particuarly by those producing nascent hydrogen.

In connection with alkaline sulphides, it is first transformed into the sulphide of arsenic which then dissolves in an excess of the reagent with the production of thioarsenites, or in certain cases, where polysulphides are used, the resultant products are thioarsenates.

ARSENIC DISULPHIDE.

The chemical formula for this compound is As_2S_2, and its molecular weight is 214.04. This compound is soluble in the sulphides and hydrates of the alkalies. It sublimes, forming an orange-colored solid.

FUNCTION IN PYROTECHNICS.

At the present time, arsenic disulphide is only used in smoke-tracer composition for rockets, in which it is combined with potassium nitrate and sulphur. We find that certain manufacturers use a composition containing saltpeter 18 parts, sulphur 15 parts, disulphide of arsenic 12 parts, while others use a mixture of 32 parts of saltpeter, 22 parts of sulphur and 32 parts of disulphide of arsenic. In these compositions, it may be assumed that the saltpeter and sulphur react, liberating sufficient heat to volatilize the disulphide of arsenic, which passes out from the openings in the containers in a gaseous form, condensing immediately upon contact with the cold air, to a cloud of dense yellow smoke. It owes its efficacy to the fact that it is sufficiently stable to withstand the temperature without decomposition, until volatilized.

SPECIFICATIONS.

It is extremely difficult to make a set of specifications which shall apply to a product prepared by grinding native realgar. The samples examined contained only small amounts of foreign materials, principally silica and garnets, as has been indicated. It is more than likely that material containing several times the amount of foreign substances would still give satisfactory results. Those long experienced with compressing compositions containing potassium nitrate, sulphur and charcoal, emphasize the danger which exists if sand or gritty material is present. These particles of sand may be rubbed together by the compression, thus rendering spontaneous combustion possible. Of course, this will apply also to the compression of the smoke-tracer composition, and for this reason the presence of sand or grit is to be avoided. However, sand or grit would not be as dangerous in connection with the smoke-tracer composition as it would be in other compositions where the percentage of potassium nitrate is higher. This is a matter which can be determined by practical experience only, and consequently we shall make no attempt at the present time to set any limit on the dirt or grit which the ground native mineral may contain.

SPECIFICATIONS FOR MANUFACTURED DISULPHIDE OF ARSENIC.

No. 1. The material shall contain not less than 90 per cent. of As_2S_2.
No. 2. The material shall be a dark-orange color, of the shade known as aurora red.
No. 3. The material should be odorless.
No. 4. When compounded the material should be ground so that all will pass through a 60-mesh sieve.
No. 5. The material shall contain not more than 0.4 per cent. moisture.
No. 6. The material shall contain not more than 1 per cent. of As_2O_3.
No. 7. The material shall contain not more than 5 per cent. of free sulphur.

CHAPTER VIII.

ALUMINUM.

HISTORY.

The name of this metal is derived from " Alumen," a term applied by the Romans to all bodies of an astringent taste. Pott, in 1746, stated that the basis of alum is an argillaceous earth, and in 1754 Marggraf pointed out the distinction between alumina and lime and its presence in combination with silica in clay.

Davy, in 1807, having isolated the alkali metals by electricity, endeavored unsuccessfully to reduce alumina in the same manner.

Oersted, in 1824, prepared aluminum chloride by passing chlorine over a mixture of alumina and carbon heated to redness. He appears to have reduced the chloride to the metallic condition by heating with potassium amalgam. The amalgam produced oxidized rapidly in the air, but left on volatilizing the potassium a tin-white metal.

· Wöhler, in 1827, having failed to procure the metal by Oersted's method, obtained it by the decomposition of the anhydrous chloride with potassium as a gray powder, which became brilliant over the burnisher.

Bunsen and Deville, in 1854, independently obtained the metal by the electrolysis of the fused chloride. Deville, in the same year, much simplified the manufacture by substituting sodium for the more expensive potassium. In 1854 he was installed in a manufactory at Javel by the Emperor Napoleon III. and supplied with the necessary apparatus for experiments on a large scale. Afterward his process was removed to Nanterre and finally to Salindres. Specimens of the metal produced by him were shown at the Paris Exhibition of 1855.

Shortly after the publication of these results, Messrs. Dick and Smith, under the direction of Dr. Percy, prepared aluminum by the action of sodium on the then newly dis-

covered mineral, cryolite, some of the product being shown by Faraday at the Royal Institution in March, 1855.

About six months subsequently, Rose independently prepared it in the same manner and published his results in an extended article in the Philosophical Magazine.

Deville at once turned his attention to this process, but on account of the impurities of the metal produced, he preferred the double chloride of aluminum and sodium, using cryolite as a flux only. F. W. Gerherd, in 1859, started the first plant for the manufacture of aluminum at Battersea, London. Some of the material produced was shown at the Society of Arts Exhibition in 1860. In 1863, Bell of New Castle, using Netto's process, also prepared aluminum and aluminum bronze. This process consisted in the use of a mixture of common salt with an equal weight of cryolite. The charge, consisting of 200 pounds, was brought to fusion, when sodium was gradually added to the amount of 40 pounds. This charge contained but 5 percent. of aluminum and less than one-half of this amount was obtained in the yield.

After a period of 11 years this method of manufacture was discontinued. Then Grabau's process, described in the Journal of the Society of Chemical Industry, was used. In this process aluminum fluoride was treated with metallic sodium. The process soon proved to be of small commercial value, so that, up to 1883, no satisfactory process had been created for the commercial production of this most important metal. Even in 1885, the total production of aluminum in the United States did not exceed 250 pounds. In 1885, it was discovered that when very small amounts of aluminum were added to iron and steel, certain very desirable qualities in these metals were produced, and this became a stimulus for further attempts to prepare aluminum on a large commercial scale. When Castner's process for the preparation of sodium by means of electrolysis was successfully attained, the thoughts of investigators turned toward the production of aluminum by the electric current. Various methods were tried and it was discovered that the application of electricity for purposes of heating and reducing metals would probably solve the problem.

In 1888, the Hall process was brought out in this country and the history of the aluminum of modern times dates from the application of that process. Before this time, aluminum was a comparatively rare metal. It was exhibited in small pieces in museums as one of the rare metals.

The following table shows the production, imports and exports of aluminum in the United States, for the years 1902 to 1917, inclusive, according to Mineral Industry 1917.

Production, imports and visible supply of aluminum in the United States.

Year.	Production.		
	Pounds.	Value.	Per pound.
1902	7,300,000	$2,284,590	$0.31
1903	7,500,000	2,325,000	.31
1904	7,700,000	2,233,000	.29
1905	11,350,000	3,632,000	.32
1906	14,350,000	5,166,000	.36
1907	26,000,000	10,920,000	.42
1908	13,000,000	4,095,000	.315
1909	15,000,000	3,345,000	.223
1910	12,000,000	2,736,000	.228
1911	[1] 28,600,000	5,720,000	.20
1912	[1] 40,000,000	9,200,000	.23
1913	[1] 64,900,000	13,600,000	.21
1914	[1] 90,000,000	16,740,000	.186
1915	[1] 99,000,000	31,581,000	.319
1916	[1]139,000,000	47,260,000	.34
1917	[1]200,000,000	74,000,000	.37

Year.	Imports.		Manu-factures.	Exports (value).	Visible supply [2] (pounds).
	Crude.				
	Pounds.	Value.			
1902	745,217	$215,032	$3,819	$116,052	8,045,000
1903	498,655	139,298	4,273	157,187	8,000,000
1904	515,416	128,350	478	166,876	8,216,000
1905	530,429	106,108	33	290,777	11,880,000
1906	770,713	154,292	1,866	364,251	15,121,000
1907	872,474	181,351	1,124	304,938	26,872,000
1908	465,317	80,268	2,334	330,092	13,465,000
1909	5,109,843	745,963	12,878	567,375	20,110,000
1910	12,271,277	1,844,830	(³)	949,215	24,271,000
1911	[4] 4,173,308	598,272	[4]63,899	1,158,603	32,773,000
1912	22,759,937	3,092,889	428,182	1,347,621	62,760,000
1913	23,185,755	3,905,977	1,090,229	966,094	88,086,000
1914	16,241,340	2,729,383	1,308,036	1,546,510	106,241,000
1915	8,534,834	1,511,988	301,863	3,682,117	107,535,000
1916	6,646,385	1,729,298	55,864	15,419,134	145,646,000
1917	58,703	18,084	57,461	14,586,467	[5] 200,059,000

[1] Estimated.
[2] Production plus imports.
[3] Not reported.
[4] From July 1 only.
[5] Included 9,470,206 pounds of ingot metal and alloys and 550,198 pounds of plates and sheets, valued at $4,571,193 during the last half of the year.

OCCURRENCE IN NATURE.

Aluminum is not found in the metallic condition in nature; it is strictly a manufactured product. The most important minerals of aluminum are Cryolite, which is a sodium-aluminum fluoride, having the formula $AlNa_3F_6$, and Bauxite, which is the hydrated aluminum oxide, having the formula $Al_2O(OH)_4$. These two minerals are the source of aluminum manufactured for commercial use. In addition to these two minerals, aluminum is found in other minerals of considerable commercial importance; corundum, of which the sapphire, ruby, and emerald are examples, are all the oxide of aluminum, having the formula Al_2O_3, colored by small amounts of other metallic oxides. With the exception of the diamond, these are the hardest of all minerals. Disapore, which is another hydrated alumina, having the forumla $AlO(OH)$; gibbsite, having the formula $Al(OH)_3$; alunogen, which is the sulphate of aluminum, having the formula $Al_2(SO_4)_3+18H_2O$; aluminite, a hydrated sulphate of aluminum, having the formula $Al_2(OH)_4SO_4$; alunite, commonly known as alum stone, with the formula $K(AlO)_3(SO_4)_2-3H_2O$; turquoise, having the formula $Al_2(OH)_3PO_4H_2O$; wavellite, having the formula $Al_6(OH)_6(PO_4)_4-9H_2O$; lazulite, having the formula $(Mg.Fe.Ca.)Al_2(OH)_2(PO_4)_2$, and chrysoberyl, having the formula $GlAl_2O_4$.

Aluminum in the form of complex silicates in various clays is widely distributed in nature in enormous quantities.

METHOD OF MANUFACTURE.

The method of manufacture of aluminum, since the introduction of the Hall process in 1888, has been exclusively the electrolysis of the oxide of aluminum, dissolved in a molten solvent, in apparatus suitably arranged for the purpose, the carbon of the electrodes combining with the oxygen of the dissolved alumina under these conditions. The requirements for the solvent are: first, that it shall be fusible at a sufficiently low temperature; second, that while in a fused condition it shall possess a high electrical conductivity; and third, that it shall be of such a nature as to avoid the

contamination of the aluminum produced with impurities. Various combinations have been tried for this purpose, the basis of all of the practical ones being cryolite, which may be brought to fusion at a temperature below 1,000° C. and when fused will dissolve from 15 to 20 per cent. of its weight of alumina. In this condition, the bath containing the dissolved alumina will have a resistance of about 2.3 volts.

Bauxite is the hydrated oxide of alumina. The operation is conducted in carbon-lined pots which form the negative electrodes. The cryolite that forms the bath is placed in the bottom of the cavity in these pots, and the carbon positive electrodes are lowered until they touch the carbon lining, and the current is turned on. In the pot the cryolite melts when red hot in the vicinity of each carbon electrode, and additional cryolite is then thrown around the carbons. In an hour or two sufficient cryolite has been melted to form a bath and the carbon anode is gradually separated from the cathode lining. The alumina is now ready to be added. This is first sprinkled on top of the bath and after it has become hot and perfectly dry it is stirred in. Adding the alumina increases the amperage, and the dissolved alumina immediately begins to electrolyze. Powdered carbon, formed from the stub ends of used electrodes which have been ground up, is placed on top of the bath to a thickness of one inch. This serves to hold the temperature and reduces radiation. The carbon electrodes are clamped to a copper bar extending the whole length of the pot, and if one part of the bath becomes cooler than it should, the carbons are crowded together at that point and it is soon heated up. In practice the ends of the carbons are kept about three-quarters of an inch from the lining, and each carbon carries about 250 to 300 amperes. When the carbons are consumed they must be replaced. The consumption of carbon in regular running is less than one pound for each pound of aluminum produced, showing that they are burnt according to the reaction $Al_2O_3 + 3C = 2Al + 3CO$, in which 102 parts of alumina would require 36 parts of carbon to combine with its oxygen, producing 54 parts of metal. If the voltage rises to 10 or more, it indicates that the alumina in the bath has become exhausted. The rise of this voltage is occasioned by the fact that the alumina added has high electrical conductivity, while the

cryolite bath has a low electrical conductivity. The increased voltage causes an electric signal lamp to light, whereupon the workmen at once stir in additional alumina. This causes the voltage to fall and the lamp goes out. When the aluminum has accumulated in the bath for several hours, it is removed with iron ladles which have been previously rubbed with chalk to keep the metal from sticking to the iron. The crude metal is remelted in large crucibles and finally cast into ingots.

The mineral bauxite contains many impurities which render its direct use impossible. Alumina is prepared from it according to the method devised by Dr. K. J. Bayer, which consists of the following procedure:

The bauxite is fused with sodium carbonate or sulphate, and the solution obtained by leaching, containing sodium aluminate, is not decomposed by carbonic acid, as was formerly the practice, but by the addition of aluminum hydrate with constant stirring. The decomposition of the solution goes on until the molecular quantity of alumina remaining in solution is to the sodium protoxide as 1 : 6. This precipitation takes place in the cold; the aluminum hydrate that separates out is soluble in acids. The alkaline solution remaining is concentrated by evaporation, taken up by ground bauxite, dried, calcined, and melted, and thus goes through the process again. The use of this caustic-soda solution containing alumina is thus much more profitable than using soda, because by using the latter only 75 per cent. of the bauxite is utilized, whereas by the former all the alumina dissolved by the solution is finally obtained. At the present time the bauxite is decomposed with a solution of NaOH, gravity 1.45, which is heated with steam under 75 to 80 pounds pressure.

To bring the alumina into a suitable physical condition for use in the reduction furnace, it must be calcined at 1,200° C. so that it shall contain no moisture when added to the molten bath. The calcined product also will not absorb moisture when exposed to the air. The electrodes used in the reduction furnaces are usually made from oil-coke, carefully selected, ground, calcined, and subjected to high pressure with the admixture of tar to act as a binder. They are then baked at about 1,200° C.

In the manufacture of the aluminum dust and flake aluminum from the metallic aluminum thus prepared, superheated steam at high pressure is forced through specially designed nozzles which open a short distance below the surface of a bath of the molten metal. The steam escaping through these nozzles tears the molten metal into very fine particles which it blows away from the surface in cones of fine spray. The coarser particles of this spray are then settled through cyclone separators and the finer particles are removed in especially designed dust chambers where the accompanying gases are filtered through canvas. After screening, the finer portion is used in certain pyrotechnic compositions as aluminum powder, and the coarser particles are ground in a Ball mill, after adding certain fatty or oily substances as binding agents to prevent the formation of dangerous dust during the grinding or flattening operation. Water cannot be used in connection with this grinding or flattening process in the Ball mill as it has been found that chemical action takes place whereby a very troublesome amount of hydrogen is produced. The treatment in the Ball mill lasts for several hours and results in the flattening out of each fine particle so that the surface exposed is greatly increased. This process yields the aluminum flake or bronze as it is known in pyrotechnic practice, and in the paint industry.

AVAILABILITY OF SUPPLY.

There are enormous deposits of bauxite in the United States and elsewhere, which can be mined very cheaply and from which aluminum can be produced in great quantities at a low cost. There are cryolite deposits at Ivigtuk, Greenland, which are enormous and almost inexhaustible. It is mined to some extent in the United States at Linwood, Ga., and Piedmont, Ala.

USES OTHER THAN IN PYROTECHNICS.

Aluminum has many great and valuable uses other than in pyrotechnics. As the metal, it has a wide use in various forms of cooking utensils, and as a constituent of alloys it is used in automobile engines. Automobile bodies are also made

of the metal. On account of its light weight it enters into the composition of the alloys in aëroplane engines. On account of its very great affinity for oxygen, aluminum is used in the application of "thermite" as a means of reducing oxides in the production of iron, manganese, chromium, nickel, cobalt, titanium, boron, molybdenum, tungsten, vanadium, and other metals. It is used as a pigment in silver bronze; alloyed with from 2 to 10 per cent. of magnesium it forms the alloy known as magnalium, the properties of which seem to offer posibilities in some pyrotechnic compositions. The true aluminum bronzes consist of copper and aluminum alone, although there are many other alloys which are termed bronze alloys, most of which also contain aluminum.

Compounds of aluminum have many valuable uses in the arts. The oxide of aluminum, commonly known as alumina, in its various forms is used in the lining of basic converters, Siemans-Martin furnaces, in the manufacture of alum, and in the ceramic industry. For the production of lakes in dyeing, aluminate of soda is used. It is used in medicine usually in the form of alum, on account of its astringent properties. In the form of silicates, the metal has an extremely wide application in the field of pottery and porcelain ware. The acetate of aluminum in combination with certain fatty acids forms a clear soap soluble in mineral oils, where it is used to increase viscosity. Alundum, manufactured from fused bauxite, is an abrasive used in the arts.

PHYSICAL PROPERTIES.

Color.—The commercial aluminum is a metal with the whiteness of tin. It has been obtained in crystals resembling octahedra and is very slightly magnetic. The commercial powdered aluminum presents the appearance of a dull gray metallic dust, resembling zinc dust, while the flake aluminum has a bright metallic appearance. It is interesting to note that 1 c. c. of the flake aluminum which has been settled by tapping to its maximum density, in a small cylindrical graduate, weighs 0.64 gram.

Solubility.—Aluminum is insoluble in water. The powder is soluble in hydrochloric, sulphuric, and nitric acids of almost any strength. With the nonoxidizing acids it dissolves

with the evolution of hydrogen, with nitric acid it produces an evolution of the usual oxides of nitrogen. The alkali hydroxides dissolve aluminum with the evolution of hydrogen and the formation of soluble aluminates. It is also dissolved by a concentrated solution of ferric chloride or ferric sulphate producing ferrous salts; it is slowly soluble in a solution of iodine in potassium iodide.

Hygroscopicity.— It is nonhygroscopic and does not change its appearance on exposure to the air.

Flame color.—This metal imparts no color to the flame, but when it burns it gives off an intense white light.

Fusibility.—Aluminum melts at 657° C.

Taste.—It has no taste.

Hardness.—Aluminum is a comparatively soft metal, although it has a tensile strength of about 12 tons per square inch.

Tenacity and opacity.—It is ductile and opaque.

Specific gravity.—The specific gravity is 2.66.

CHEMICAL PROPERTIES.

The atomic weight of aluminum is 27.1. It is an element and a metal. It does not change its chemical nature on exposure to the air under normal conditions. It absorbs about its own volume of hydrogen, which, however, is expelled on heating. If finely divided, it undergoes partial oxidation at 400° C.

REACTIONS.

Water has no action upon aluminum, although when the aluminum is alloyed with sodium a slight action occurs. The very great affinity which aluminum possesses for oxygen is its most characteristic property and its function in pyrotechnic compositions. When it absorbs this oxygen in the rapid combustion which takes place in pyrotechnic pieces, the oxide of aluminum is formed with the formula Al_2O_3. It is almost invariably determined quantitatively by precipitation with ammonia as the hydroxide, which is ignited to the oxide. This method, however, is not very accurate and leads to high results, owing to the fact that perfect dehydration is impossible and to the occlusion of certain impurities.

When heated with silver nitrate, metallic aluminum slowly dissolves and metallic silver is precipitated. This reaction is accelerated by using an ammoniacal solution of silver chloride. A solution of copper will react upon aluminum, causing the latter to go into solution and precipitating copper in the metallic form. Aluminum compounds are usually colorless. It is generally necessary to fuse the naturally occurring silicates and oxides of aluminum with sodium carbonate or a similar fusion mixture in order to obtain complete decomposition.

FUNCTION IN PYROTECHNIC PIECES.

The behavior of aluminum in the various pyrotechnic pieces in which it is used depends upon the materials with which it is associated. In general use, however, its function is the same in the pyrotechnic pieces as it is in the various thermite compositions in which it is generally used, namely as a reducing agent. Further, the aluminum compounds formed during oxidation do not yield distinctive flame colorations. With potassium nitrate aluminum yields potassium aluminate, $(KAlO_2)$, while with barium nitrate the compounds formed are barium oxide and alumina. Aluminum will give off more heat during combustion per unit of weight than any other metal that is practically available. This is shown in the following table which gives the heat produced by various metals on oxidation.

Heat of formation.	Calories.	Heat of formation.	Calories.	Heat of formation.	Calories.
Al_2O_3.........	392, 600	CuO........	37, 700	Na_2O.........	100, 900
$Sb_2O_3, 3H_2O$..	166, 900	H_2O.........	69, 000	SrO..........	131, 200
As_2O_3.........	154, 670	FeO.........	64, 300	SO_2 (gas)....	69, 260
BaO..........	133, 400	Fe_2O_3.......	195, 600	SnO_2.........	141, 300
Bi_2O_3.......	139, 200	PbO........	50, 800	TiO_2........	215, 600
CdO........	66, 300	MgO........	143, 400	ZnO	84, 800
CaO..........	131, 500	MnO_2........	125, 300	ZrO_2........	177, 500
CO..........	21, 160	K_2O.........	98, 200		
CO_2.........	68, 040	SiO_2........	180, 000		

Aluminum is a metal of low specific gravity, and its efficiency in giving off a large amount of heat per unit of weight makes it especially desirable for use in the pyrotechnic

pieces designed to be used in connection with aëroplanes where excessive weight is to be avoided. We find that the metal is used in two forms which are commercially known as "disintegrated aluminum or dust," and "flake aluminum or aluminum bronze." Quite often pyrotechnic compositions include both of these forms for the reason that the candle-power is thereby increased. The dust alone, however, is not as efficient as the flake, as it does not expose so large a surface to combustion per unit of weight.

It is found necessary in preparing compositions containing aluminum flake and aluminum dust to use oils, fats, or greases in order to prevent "dusting" with the accompanying danger of dust explosions and to render the compositions sufficiently adherent so that the various constituents will not separate during handling. Many different materials have been used for this, such as castor oil, vaseline, etc., and no particular stress is laid upon the advantage of any one over the others. The greatest possible care, however, should at all times be exercised in handling finely divided aluminum, as the danger from dust explosion is great and the material itself is of such a nature that the violence of such explosions is terrific.

METHOD OF ANALYSIS.

The analysis of aluminum flake or powder presents many difficulties. From its method of preparation the impurities which will be commonly found are silicon, iron, and sometimes small amounts of carbon, nitrogen, and sodium. Various methods for the determination of metallic aluminum have been suggested and used, among which may be mentioned the measurement of the volume of hydrogen liberated by hydrochloric acid or caustic soda from weight amounts of the sample. Of these methods the setting free of hydrogen by caustic soda is to be recommended for the reason that iron if present will not cause the formation of any hydrogen gas as will be the case if hydrochloric acid is used. Silicon, if present as an impurity, will detract from the accuracy of the results. Another method involves the use of ferric sulphate which is reduced by metallic aluminum to ferrous sulphate, which can be determined volumetrically by the usual titration with potassium permanganate. Here, again, the pres-

ence of iron will affect the accuracy of the result, as will also the fact that hydrogen is formed during the reaction in consequence of which the total reducing power of the aluminum is not represented by the amount of ferrous salt produced. For practical purposes the sodium, nitrogen, and carbon impurities may be disregarded.

The following methods of analysis are based on the assumption that the material examined is the ordinary commercial product of the usual grade of purity.

Moisture.—Not less than 3 grams shall be spread out on a watch-glass and dried to constant weight at a temperature of 100° C. The loss in weight shall be reported as moisture and when divided by the weight taken will give the percentage.

In the following determinations of silicon, iron, and aluminum, material shall be used from which the oils, fats, and greases have been extracted by ether as described in the oil, fat, and grease determination, and from which all the ether has been removed by heating at a temperature of 100° C. for one hour.

Silicon.—An acid mixture shall be prepared consisting of 400 c. c. of concentrated nitric acid, 1,200 c. c. of concentrated hydrochloric acid, 600 c. c. of concentrated sulphuric acid and 1,800 c. c. of water. One gram of the sample shall be treated with 35 c. c. of this acid mixture in a 4½ inch porcelain casserole with a 5-inch watch-glass as a cover. When the sample is dissolved, the solution shall be evaporated not only to fumes but to dryness and baked. This will remove all the nitric acid and hydrochloric acid and will bring about the complete dehydration of the silica. When cool 10 c. c. of 25 per cent. sulphuric acid and 100 c. c. of water shall be added, the solution boiled and filtered, and the residue well washed and ignited. This residue shall then be fused with from 8 to 10 times its weight of sodium carbonate, and then digested in a porcelain casserole with sulphuric acid (1:1). The solution carrying the silica shall be evaporated until it fumes. The solution shall then be carefully diluted, boiled, filtered, and the residue well washed and ignited in a platinum crucible and weighed. A few drops of hydrofluoric acid and two drops of concentrated sulphuric

acid shall be added, and the crucible gently heated until the acids have evaporated, care being taken to avoid loss by spattering. The crucible shall then be ignited; the loss in weight is silica. This loss in weight multiplied by the factor 0.4693 will give the silicon content in the sample. This weight when divided by the weight taken will give the percentage of silicon.

Iron.—A 250 c. c. Erlenmeyer flask shall be cleaned, dried, and allowed to stand on the pan of the balance until it reaches constant weight. The aluminum powder or flake to the amount of approximately 1 gram shall be introduced into the flask which is then weighed. This method of weighing out the sample to be analyzed is recommended for the reason that it is extremely difficult to transfer the powder or flake aluminum, as fine particles stick very tenaciously to any glass surface which they may touch. The flask shall then be closed with a one-hole rubber stopper containing a glass delivery tube which shall in turn be connected with a Drexel gas-washing bottle containing a small amount of water to serve as a trap. The cork is then removed and 25 c. c. of 1:5 sulphuric acid are introduced. The flask is closed with the stopper, and the contents gently heated. The evolution of hydrogen soon begins, and as the reaction is violent and accompanied by the liberation of much heat, it is important to have a dish of cold water at hand in which the flask may be cooled in the event that the reaction becomes too violent. Finally the contents shall be heated to gentle boiling in order to dissolve the last of the aluminum. When the reaction is complete, the contents of the flask shall be diluted, after cooling, with previously boiled cold water, and the iron, which will be present in the form of ferrous sulphate, shall be titrated with an approximately one-tenth normal solution of potassium permanganate whose available oxygen content is known. The reaction between the potassium permanganate and the ferrous sulphate contained in the solution is expressed by the equation:

$$10FeSO_4 + 8H_2SO_4 + 2KMnO_4 =$$
$$5Fe_2(SO_4)_3 + K_2SO_4 + 2MnSO_4 + 8H_2O$$
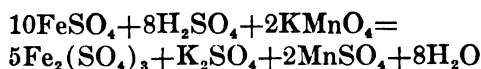
Under acid conditions, potassium permanganate furnishes available oxygen according to the reaction:

$$2KMnO_4 + 3H_2SO_4 = K_2SO_4 + 2MnSO_4 + 3H_2O + 5O$$

From a consideration of these two reactions, it will be seen that $10FeSO_4$ is equivalent to $2KMnO_4$, which in turn is equivalent to $5O$, or two atoms of iron are equivalent to one atom of oxygen. These two atoms of iron have a total atomic weight of 111.68 and oxygen has the atomic weight of 16, consequently the weight of available oxygen consumed during the titration, multiplied by the fraction $\frac{111.68}{16}$ or 6.98, will give the weight of metallic iron in the sample, and this weight, divided by the weight of the sample, will give the percentage of its metallic-iron content.

Aluminum.—It is evident that the processes used in the manufacture of both aluminum dust and flake aluminum may cause the production of varying amounts of the oxide which will detract from the efficiency of the material. For pyrotechnic purposes the reducing power of the aluminum measures its value, and the fact that the metal contains small amounts of the impurities which have been mentioned, will have but little effect upon its desirability. A method, therefore, which shall afford a rapid and accurate determination of this reducing power which may be expressed in terms of metallic aluminum, is very desirable.

After a long series of experiments it was found that the reducing power of the aluminum dust or flake on litharge, PbO, can be easily determined by fire assay.

It was found that the accuracy of the determination depended upon two factors. First, upon the formation of a well-balanced liquid slag, and, second, upon the temperature at which the assay was run.

It was found convenient to make these assays in what are known as 25-gram fire-clay crucibles; a charge of 3 grams of metallic aluminum proved to be an appropriate amount for the determination. The aluminum reacts with the litharge according to the equation

$$2Al + 3PbO = Al_2O_3 + 3Pb$$
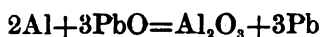
These two atoms of aluminum have the total atomic weight of 54.2, while three molecules of lead oxide have the total molecular weight of 669.6; consequently the weight of metallic aluminum used, multiplied by the fraction $\frac{669.6}{54.2}$ or 12.35 will give the amount of litharge which the aluminum is capable of reducing. In the case of the 3-gram charge, this weight of litharge is 37.05 grams.

After a number of experiments it was shown that a charge consisting of 3 grams of aluminum mixed with 100 grams of litharge and 30 grams of borax glass, $Na_2B_4O_7$, with a cover of 25 grams of borax glass, yielded an amount of slag which was convenient to handle and of such a nature that it fused readily, forming a very liquid mass which could be easily and cleanly poured out of the crucibles.

These fusions were conducted in a gas muffle heated to such a temperature that the dividing line between the end of the muffle and its bottom could not be seen. The fusions required 20 minutes after the crucibles were placed in the preheated muffle. After the 20 minutes had elapsed the melted mass was poured from the crucibles into the usual conical slag mold used by assayers. In these molds, the molten lead, being the heaviest material present, settles to the bottom. After cooling, the lead buttons break away easily from the slag, which is brittle, slightly yellow, almost transparent and glassy in character. Finally the lead buttons were pounded into cubes to remove adhering particles of slag and were then weighed. The accuracy of the results was found to depend upon the temperature at which the fusions were made, the requirement being that a high temperature should be used throughout in order that the time required might be short.

From the equation it may be seen that two atoms of aluminum, having the total atomic weight of 54.2, are equivalent to three atoms of lead having a total atomic weight of 621.6; consequently, the weight of the lead obtained, multiplied by the fraction $\frac{54.2}{621.6}$, or 0.0872, will give the weight of the equivalent amount of aluminum, and this weight divided by the weight taken will give the percentage of aluminum in the sample.

It should be noted that this method permits the use of a comparatively great weight of aluminum, and, further, that the weight of the lead produced, being approximately 12 times that of the aluminum, contributes to the accuracy of the results. The method is quick, easy, and accurate from a practical standpoint.

Fats, oils or greases.—About two grams of the flake aluminum shall be weighed out in a 250 c. c. Erlenmeyer flask, as described under iron. Fifty cubic centimeters of anhydrous ether shall then be added and the flask thoroughly shaken for some time. The ether shall then be decanted through a filter, receiving the filtrate in a clean, dry beaker. The aluminum in the flask and the filter shall then be washed five times with small portions of fresh ether. The combined ethereal filtrates shall be evaporated to a low volume in the beaker by gentle heating on a steam bath, and when the volume shall have been sufficiently reduced the liquid shall be transferred to a weighing bottle, whose weight has been previously determined, and evaporated to dryness, finally heating to a temperature of 70° C. for one hour. The residue from the evaporation will contain the fats, oils, or greases of the metallic powder, and when its weight is divided by the weight of the sample taken the percentage of oils, fats, or greases is obtained.

In Richards's book on aluminum, edition of 1896, page 606, it is stated that commercial aluminum may contain silicon, iron, lead, tin, zinc, copper, silver, carbon, sodium, chlorine, and fluorine.

The methods outlined above include all the determinations which are usually necessary from a practical standpoint. If, however, it is desired to determine the other constituents, the following methods given by Richards may be used.

Lead.—Dissolve the aluminum in hot hydrochloric acid, evaporate to dryness, moisten with hydrochloric acid add hot water and boil. Filter hot to separate out silica. To the hot boiling solution add a few drops of sulphuric acid and let stand an hour. The precipitated lead sulphate can then be filtered out and weighed.

Copper.—Dissolve the aluminum in hot hydrochloric acid, add ammonia in slight excess and boil. Filter and wash; the filtrate will be blue if any copper is present. In order to determine the amount of copper, evaporate this filtrate to dryness, take up with a little hydrochloric acid and determine the copper by any ordinary method; or the ammoniacal copper solution may be acidified with sulphuric acid, crystals of oxalic acid added, the liquid boiled and the copper, deposited as oxalate. This is washed with boiling water, dried, calcined, gently ignited, and weighed as cupric oxide. The ammoniacal copper solution might also be acidified with acetic acid and the copper precipitated by lead foil.

Zinc.—Dissolve the aluminum in hydrochloric acid; evaporate to dryness, heat for one hour at 120° C., and take up the residue with strong acetic acid; filter off the separated silica. On passing sulphureted hydrogen through the solution, zinc will be preciptated free from aluminum or iron. The precipitated zinc sulphide is washed carefully with distilled water saturated with sulphureted hydrogen, dried, calcined very carefully in a muffle and afterward very strongly over a blast lamp and weighed as zinc oxide. If the sample analyzed contains copper or lead the zinc oxide will be contaminated with these two metals, in which event it must be purified by the usual methods of separation.

Tin.—A solution of aluminum in hot nitric acid will leave the tin as insoluble meta-stannic acid. This residue is washed and treated with warm hydrochloric acid which dissolves the tin compound, leaving the silica. The tin is then thrown down in the solution of stannic chloride by sulphureted hydrogen. The stannic sulphide obtained is ignited gently, moistened with nitric acid, ignited more strongly and the tin weighed as stannic oxide.

Silver.—Dissolve the aluminum in weak aqua-regia, dilute and filter out the siliceous residue which will contain also all the silver as chloride. Wash carefully, and then dissolve out the silver salt with concentrated ammonia. On neutralizing the ammoniacal solution with nitric acid, the silver chloride is again precipitated, washed by decantation, dried at 250° to 300° C. and weighed.

Sodium.—The metal is dissolved in pure hydrochloric acid, evaporated to complete dryness in a platinum dish and the insoluble siliceous materials filtered off. The solution is mixed with a large excess of nitric acid, evaporated in a porcelain dish, covered by a watch-glass, thus converting the bases into nitrates which are then transferred to a platinum dish. Here the solution is evaporated to dryness and calcined lightly on the sand bath. Cool and moisten with a solution of ammonium nitrate, containing free ammonia. Heat until all odor of ammonia has disappeared. Take up with water and wash the insoluble portion by decantation through a filter. To the solution a drop of ammonium oxalate is added which sometimes precipitates a trace of calcium, indicative of the presence of fluorspar in the slag with which the metal may be contaminated. After filtering, it is necessary to evaporate to dryness in a weighed platinum dish, cover and heat to 200° C. to decompose the ammonium nitrate. Nitrate of soda remains. This is moistened with water and on it are placed several crystals of oxalic acid. Dry, calcine, and there remains sodium carbonate which is often impregnated with a little carbon from the decomposition of the sodium oxalate. Dissolve the residue in water; if not clear, filter, mix the solution with a little hydrochloric acid, evaporate to dryness, heat to 200° C. and weigh as sodium chloride. Commercial aluminum rarely contains metallic sodium, but when it does exist, it can usually be detected from the fact that the amount of chlorine present is not sufficient to combine with the sodium found. The presence of fluorine would weaken this conclusion, but it is seldom present in any quantity.

Chlorine.—Dissolve the aluminum in chlorine-free caustic soda, neutralize with nitric acid in very small excess, filter and add several drops of nitrate of silver. The chloride of silver precipitated is washed and dried at 300° C. and weighed.

Carbon.—One gram of aluminum powder is placed in a porcelain boat and introduced into the combustion tube of an ordinary combustion furnace. The aluminum and carbon are then burned in a current of dry oxygen. The carbon dioxide formed is absorbed in caustic soda in any standard absorption apparatus convenient, and weighed.

Fluorine.—No quantitative method is given for the determination of fluorine. In aluminum powders its presence will be due only to the accidental inclusion of slag with the metal, which is extremely improbable.

Titanium.—Dissolve two grams of the aluminum in caustic alkali solution. Bring to boiling and filter quickly, washing rapidly with boiling water. The residue contains all the iron and titanium. Dry and fuse with eight grams of potassium-acid sulphate. After a complete fusion, taking perhaps 30 minutes, dissolve in hot water and filter out the silica. To the solution add dilute ammonia until a slight precipitate forms. Add dilute sulphuric acid until the precipitate just redissolves. Then add four drops of concentrated sulphuric acid, dilute to 250 c. c. and saturate with sulphurous-acid gas. Heat slowly to boiling and boil gently for 45 minutes, occasionally adding a little strong sulphurous-acid water. Filter off the precipitated metatitanic acid, wash thoroughly with hot water, dry, ignite and weigh as TiO_2.

ANALYTICAL RESULTS.

The sample of flake aluminum analyzed as an example was from a commercial lot.

Moisture:

	Grams.
Weight taken	3
Weight after drying	2. 9769
Loss in weight	. 0231

This divided by the weight taken gives 0.77 per cent.

Silicon:

	Gram.
Weight taken	1
Loss by HF	. 007

This multiplied by the factor 0.4693 gives 0.0033 grams; divided by weight taken gives 0.33 per cent.

Iron:

	Gram.
Weight taken	0. 9307

Volume of permanganate solution used 1.3 c. c. Number of cubic centimeters of permanganate taken multiplied by the oxygen equivalent of the permanganate, which was 0.000758 gram per c. c., gives 0.0009854 gram oxygen; this

multiplied by the factor 6.98 gives 0.0068 gram iron; this divided by the weight taken gives 0.73 per cent. of iron.

Aluminum:

	Grams.
Weight taken in each case	3
Weight lead button	33. 580
Weight lead button	33. 818
Weight lead button	33. 645
Weight lead button	33. 480
Weight lead button	33. 683
Weight lead button	33. 568
Weight lead button	33. 567

Weight aluminum obtained:

	Per cent.
2.9282 grams	97. 61
2. 9489 grams	98. 29
2. 9338 grams	97. 79
2. 9195 grams	97. 32
2. 9371 grams	97. 90
2. 9271 grams	97. 57
2. 9270 grams	97. 57

Fats, oils, and greases:

	Grams.
Weight taken	1
Weight weighing bottle plus fats, oils, and greases	12. 4690
Weight weighing bottle	12. 4490
Weight oils, fats, and greases	. 0200

Equals, 2 per cent.

DISCUSSION OF RESULTS.

From the appearance of the flake aluminum in which the moisture was determined, it is scarcely conceivable that it should contain as much moisture as the results indicated. It is probable that a part of the oils, fats, and greases which the material contained were driven off at the temperature used in the moisture determination. Later, when the oils, fats, and greases themselves were determined, the material in the weighing bottle seemed to have quite a pronounced odor, indicating that there may have been a partial loss in weight by volatilization.

SPECIFICATIONS.

The aluminum flake and dust to be used for pyrotechnic purposes should be in accordance with the following specifications:

The material shall be of the same purity as commercial ingot aluminum, except for such small amounts of aluminum oxide as may be produced during its manufacture. The amount of this aluminum oxide, however, should not be greater than 1 per cent.

1. It shall contain not less than 95 per cent. of metallic aluminum in the dried sample from which oils, fats, and greases have been removed.
2. It shall not contain more than 1 per cent. of moisture.
3. It shall not contain more than 2 per cent. of fatty substances.
4. It shall not contain more than 1 per cent. of iron calculated as the metal.
5. It shall not contain more than one-half of 1 per cent. of silicon.
6. The powdered aluminum or aluminum dust shall all pass through a 100-mesh sieve of standard make.
7. The flake aluminum shall be manufactured from powdered aluminum of such a degree of fineness that it shall all pass through a standard 50-mesh sieve, by treatment in a Ball mill for at least five hours, running at the speed specified by the manufacturers of the machine.
8. It shall be so flattened as to be the equal in fineness to the ordinary commercial flake aluminum used for bronze paints.

POTASSIUM CHLORATE.

Count Claude L. Berthollet in 1786 discovered potassium chlorate. He showed how it could be prepared in the pure state, and he investigated and later described the properties of this compound. The salt was known to Glauber, but it was not prepared by him in a pure condition, nor did it receive any attention until Berthollet prepared and purified it. He found that potassium chlorate, if substituted for saltpeter in gunpowder, produced a more violent explosive, and in 1788 it was his intention to manufacture gunpowder by substituting it for saltpeter.

The first attempt, however, proved very disastrous. A party had been made up to visit the new powder mills in order to examine the first product. This party included, among others, an engineer, M. Lefort, and Mlle. de Chevraud. While the mixture was being incorporated in a stamp mill the party went to breakfast. M. Lefort and Mlle. de Chevraud were the first to return, and as they entered the plant the charge exploded with violence, throwing them a great distance and inflicting injuries so severe that they both died in a few minutes.

Subsequently, repeated attempts were made to prepare a propulsive explosive with the use of a chlorate, but on account of the fact that the explosion is uncontrollable and apt to be too violent, it has never been successfully accomplished.

It was not until 1897, with the invention of cheddite, that chlorate mixtures could be used with safety, even as blasting explosives. This compound was invented by E. A. G. Street, and consists of potassium chlorate mixed with castor oil, in which aromatic nitro compounds are dissolved. The great sensitiveness of other chlorate mixtures is largely overcome, and when potassium chlorate is incorporated with the compounds just described, it has been found to be of con-

127

siderable value, and is used largely in England, France, and Germany.

In 1895 Cundill and Thomson, in their Dictionary of Explosives, submitted descriptions of potassium chlorate in 150 mixtures, but none of these have proved to be of practical use, with the exception of a few cap and fuse compositions.

A favorite mixture, in which potassium chlorate has been substituted for saltpeter, consists of potassium chlorate 50 parts, potassium ferrocyanide 25 parts, and sugar 25 parts. This mixture is known as "white gunpowder." The violence of its explosion is great, but it is very sensitive, and it is therefore classed as extremely dangerous. Mixtures of a chlorate with a sulphide or sulphur are specially sensitive.

It is, therefore, to be expected that the history of gunpowder, in so far as the use of a chlorate is concerned, is a long line of disasters. Such mixtures are used for percussion caps and other purposes where high sensitiveness is required.

The use of chlorates in colored lights and other similar fireworks will be treated more fully under the chapter on the function of potassium chlorate in pyrotechnics.

Suffice it here to say that chlorate mixtures are forbidden in England, and in many compositions in the United States. It has been found by using various substances in connection with a chlorate that blasting explosives could be made which are not more dangerous than other explosives. Perchlorates have been substituted for chlorates, and their use is rapidly extending on account of their being less sensitive and, therefore, safer than the chlorates. Sodium chlorate is more dangerous in mixtures than is potassium chlorate, as it is a deliquescent compound, causing segregation of fine crystals, due to subsequent efflorescence, which constitutes an additional factor of danger during handling and storage.

Chlorate of potash by itself, unmixed with combustible matter, is not classed as dangerous under ordinary circumstances, but it might be appropriate to mention that, on May 12, 1899, a large quantity of potassium chlorate exploded during the progress of a fire in the works of the United Alkali Co., at St. Helens, which did an enormous amount of

damage. The result of this explosion led to a more thorough examination of the behavior of potassium chlorate under heat. Berthollet had already shown that if it was subjected to a blow combined with sudden intense heat it exploded.

Dupré showed that heat alone is sufficient to explode chlorate if it be applied with sufficient suddenness. A bead of potassium chlorate supported in a loop of thin platinum wire, when heated rapidly in a Bunsen burner, can be made to explode.

The St. Helens disaster was not the only one where large quantities of potassium chlorate have exploded in the course of conflagrations. On July 27, 1908, a similar explosion occurred on the premises of a carrying company in Manchester; on July 21, 1910, at the match works of Messrs. Bryant & May, at Seaforth, near Liverpool, a similar explosion took place. In 1912, an explosion occurred during repairs to a drying machine, in which five men were killed.

Officially, potassium chlorate is not classified as an explosive. Nevertheless, where large quantities are stored, they should be kept in a fireproof building and separated from all combustible materials. Wood and other organic matter, when impregnated with chlorate, are intensely inflammable. The explosive nature of a chlorate is due to the fact that heat is liberated when the chlorate is decomposed.

Sprengel had rendered chlorate explosives reasonably safe by separating the chlorate from the combustible matter. He made up the potassium chlorate into porous cartridges and used a liquid combustible; just before use, the former is dipped into the latter. These explosives, however, are not permitted in Great Britain, as the dipping operation is regarded as constituting a step in the process of manufaucture, and consequently may only be carried out in a duly licensed factory.

Sprengel explosives are made in France, under the name of " Explosif 03 " or " Prométhée; " the oxygen carrier, or the combustible, may be varied. An example of such an explosive consists of an oxygen carrier containing 95 per cent. of potassium chlorate, and 5 per cent. of manganese dioxide, and a combustible containing 50 per cent. of nitro-

benzene, 20 per cent. turpentine, and 30 per cent. naphtha. In these the oxygen carrier varies from 92 to 87 per cent., and the combustible material from 8 to 13 per cent.

Even with this mixture, a severe explosion took place on May 10, 1909, at St. Eusebio, near Genoa, Italy, when the manager, head foreman, a customs officer and eight workmen were killed, and three other men were injured.

Another preparation, similar to the Sprengel explosive, is known as "Rack-a-rock," and consists of cartridges of chlorate of potash, which are dipped just before use into a combustible oil. For this purpose nitrobenzene is used, or "dead oil," which consists chiefly of hydrocarbons from coal tar, or a mixture of the two. The chlorate cartridges are inclosed in small bags of cotton; before use, they are placed in a wire basket suspended from a spring balance, and dipped into a pail containing the liquid, until from a quarter to a third of the weight of the chlorate has been taken up. The chlorate sometimes contains an addition of a small per cent. of iron oxide. Considerable quantities of "Rack-a-rock" were in storage at Port Arthur and Dalny, at the commencement of the Russo-Japanese War, and were used in the earlier operations.

Prométhée is similarly used in the form of compressed cartridges, but the French Government has refused to accept it in the form of grains, as the danger of ignition by friction during manufacture and use would be greatly increased. The Government has also refused to issue it already impregnated with the combustible, as it would then possess no advantage over cheddite. However, an explosive of this sort has been introduced recently in Germany, in order to economize in the use of nitrates during the war.

If a charge of Sprengel explosive be fired with a primer of black powder, it should be so made up that admixture is impossible; this is done by making a compressed pellet of black powder wrapped in impermeable paper. The primer of black powder should be not less than 10 per cent. of the weight of the charge, with a minimum of 1 ounce.

The development of the use of cheddite has received special attention from the French Government. The principle of the cheddite mixtures, it will be recalled, is the use of chlorates with an oily material, such as castor oil thickened by having

a nitro-hydrocarbon dissolved in it. The name is taken from Chedde, the place in Haute Savoie where the firm of Bergés Corbin et Cie manufacture chlorates by electrolytic methods. It is at this place that E. A. G. Street invented the composition. It has been found necessary to keep the proportions of the various constituents within certain limits in order to produce an explosive that shall possess the right degree of sensitiveness and shall not exude oil. It was also found that the velocity of detonation of cheddite varies considerably with the density to which it is compressed. With the increase of density, the velocity of detonation rises until it reaches a maximum and then falls rapidly. This fall is due to the fact that the explosive becomes very insensitive to detonation when the density exceeds a certain critical value, and this difficulty can only be overcome to a slight extent by the use of a stronger detonator. Some of the earlier preparations were found to increase in density on keeping, and consequently to diminish in sensitiveness, but this was traced to the use of dinitrotoluene which had been insufficiently purified. The nitro-body should not melt below 60°, else there is danger of exudation. The explosives are easily compressed and therefore there is danger of diminishing the sensitiveness too much, if charges are rammed too hard in the bore hole.

Various attempts have been made to produce a satisfactory cheddite in which the potassium chlorate is replaced by the cheaper sodium salt, which contains a larger percentage of oxygen, but the mixtures first made were found to be too insensitive when the density exceeded quite a moderate amount. Moreover, sodium chlorate is very hygroscopic, and when ground gives rise to a great deal of dust, which makes the workers' clothing and similar material very inflammable. Those working with this substance in the powder works at Vonges are obliged not only to change their clothes, but to have a complete bath when they leave off work. However, it was found that a mixture containing 16 per cent. of dinitrotoluene and without nitronaphthalene could be fired up to a density of 1.65 and was more powerful than the other types.

The following cheddites are authorized in France:

	01.		02, type 60 bis m.	05.
	Type 41.	Type 60 bis.		
Potassium chlorate......................	80	80	79	......
Sodium chlorate.........................	....	....	....	79
Castor oil...............................	8	5	5	5
Mononitronaphthalene..................	12	13	1	......
Dinitrotoluene..........................	....	2	15	16
Paraffin................................	....	....	....	
Price per kilogram.............francs..	2.10	2.10	2.30	......

In making cheddite mixtures, the nitro compounds are first dissolved in the castor oil at 80° C., and the finely powdered, dry, warm chlorate is then added gradually, while the mass is stirred with a wooden rod. The incorporation of a charge of 25 kilograms lasts about 10 minutes. The material is then carried to another building where it is further mixed on a wooden board while half-cold for another 10 minutes, so as to get it in a suitable granular condition. Each particle of chlorate should be entirely coated with the oily mixture. The material is next sifted and what is too fine is added to a later charge. That which is of the corect size is made into cartridges by ramming it into wooden molds, from which it is transferred to paper cases. If the explosive contains sodium chlorate, the cases should be then dipped in molten paraffin to prevent the absorption of water: If the per cent. of moisture rises above 1 per cent. the explosive is impaired.

Cheddite is a soft yellowish material of fine grain, but is sometimes artificially colored. In consequence of its plasticity, it can easily be compressed. It is generally put up into cartridges 22 cm. long and 2.5 cm. diameter. Cheddite (41) is a slow, mild explosive, which splits rocks rather than shatters them. Cheddite (60) is more violent, and the sodium-chlorate cheddite (05), still more so. The velocity of detonation of cheddite (60) was measured by L'heure and found to be 3,175 meters per second, about half that of picric acid, and blasting gelatine and other very high explosives, and that of (02), 2,750 meters per second.

Mixtures similar to cheddite have been tried in France and elsewhere, such as (04) which is a mixture of 90 parts potassium chlorate and 10 parts of paraffin wax. Sébomite containing tallow and di nitro benzene or nitrotoluene, (06) or minelite containing heavy petroleum, mineral jelly and paraffin wax are sometimes used.

Another chlorate mixture, which has received some attention from the French Government, is known as "Steelite." It consists essentially of potassium chlorate, the particles of which are enveloped in oxidized resin. Steelite was found to possess no advantages over cheddite and has had very limited application.

In Germany, "Silesia" has been made, which consists essentially of potassium chlorate incorporated with unoxidized resin, and, to make it pass the Continental tests for safety explosives, a considerable proportion of sodium chloride is added.

The following compositions indicate the nature of steelite and silesia:

	Colliery steelite.	No. 3.	No. 5.	Silesia 1V 22.	Silesia 4.
Potassium chlorate	72.5–75.5	75	79.2	70	80
Oxidized resin	23.5–26.5	25	15.8	8	20
Castor oil	0.5– 1				
Aluminum			5		
Sodium chloride				22	
Moisture	0– 1				

The silesia explosive has a large excess of chlorate, and the gases produced contain 14.2 per cent. of free oxygen.

In Austria, a chlorate explosive called chloratit has been sanctioned for use in coal mines during the war. It is hygroscopic, however, and gives rise to bad fumes and is, therefore, very objectionable.

Chlorates should never be mixed with ammonium salts, as ammonium chlorate would be formed, and this is apt to explode spontaneously. Mixtures of chlorate with picric acid or trinitrocresol also should not be made, as they are very sensitive.

The above statements are largely quoted from Marshall on Explosives.

OCCURRENCE IN NATURE.

Potassium chlorate does not occur as such in nature to any important extent. This may properly be expected on account of the fact that it carries a high percentage of oxygen which is readily given up on contact with reducing materials, such as sulphide minerals, organic matter, etc. While most compounds found in nature carry oxygen, those which persist generally resist these reducing substances. It, therefore, is apparent that practically all of the potassium chlorate which is used must be a manufactured article. The crude material invariably used for this purpose is potassium chloride. This salt occurs in nature in a very pure condition in several minerals and may be mined from extensive deposits, as has been set forth in detail in the chapter on saltpeter.

METHOD OF MANUFACTURE.

Potassium chlorate was first made by the decomposition of hypochlorites in hot solution. Chlorine is run into potassium hydroxide; this is done in a hot and concentrated solution. Reactions take place in two stages, as indicated by the equations $2KOH+2Cl=KClO+KCl+H_2O$ and $3KClO=KClO_3+2KCl$. If this is expressed in one equation we have $6KOH+6Cl=KClO_3+5KCl+3H_2O$. On evaporating the solution the chlorate crystallizes out, as it is far more insoluble than the chloride. The salt is then purified by a further crystallization.

It will be seen by the above equations that five times as much chloride is formed as chlorate.

Another method formerly used for the manufacture of potassium chlorate involves the following steps:

Chlorine was passed into a solution containing milk of lime in suspension. The following reaction takes place:

$$2Ca(OH)_2+4Cl=Ca(OCl)_2+CaCl_2+2H_2O.$$
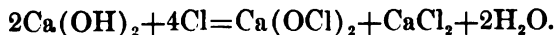
This reaction expresses in effect the formation of calcium hypochlorite, but does not attempt to take into account any intermediate compounds containing both chlorine and the hypochlorite radical which may be formed. During this operation the temperature is maintained at from 60° to

70° C. At this temperature the calcium hypochlorite is immediately transformed into calcium chlorate. According to the reaction $3Ca(OCl)_2=Ca(ClO_3)_2+2CaCl_2$.

In practice this is done in cast-iron cylinders provided with stirrers. The heat of the reaction is regulated by the rapidity with which the chlorine is admitted, so that the proper temperature is maintained within the cylinders without the use of any material amount of outside heat. Any unabsorbed chlorine is passed into another cylinder where it is utilized. Potassium chloride is then added in sufficient quantity and the solution concentrated by boiling to a specific gravity of about 1.35. The reaction takes place as follows: $Ca(ClO_3)_2+2KCl=2KClO_3+CaCl_2$. On cooling, most of the potassium chlorate crystallizes out. Successive crops of crystals are subsequently obtained by evaporation of the mother liquors. The crude potassium chlorate is purified by recrystallization and finally separated in a centrifugal machine.

These methods of manufacture are now entirely superseded by the production of potassium chlorate by the electrolysis of potassium-chloride solutions. In these reactions potassium hypochlorite is the first product, the formation of which is accompanied with the production of hydrogen, but before the hydrogen produced can completely reduce the hypochlorite, a large portion of the latter is transformed into the chlorate at the temperature prevailing in the solution. This transformation into the chlorate is accompanied by the reproduction of the chloride, which in turn is re-electrolyzed, and thus the potassium chloride is finally completely converted into potassium chlorate. Of course, the hypochlorite is subject to reduction by the nascent hydrogen at the cathode, and is further subject to decomposition at the anode with loss of oxygen, both of which represent lost efficiency; for this reason the conversion of the hypochlorite to the chlorate is made as rapidly as possible by keeping the solution hot and slightly acid. The current efficiency can be made from 85 to 90 per cent. The voltage required for the deposition of the chlorate ion is much higher than that for the chlorine or hydroxyl ion, hence a solution containing potassium chloride remains in the bath, but when all the chloride is oxidized potassium chlorate remains.

In practice it is customary to electrolyze the solution of potassium chloride at a temperature of not less than 70° C., the heat being produced by using a high-current density which also gives a high yield per plant unit. At this temperature, the substances primarily formed at the anode are very destructive to most anode materials.

Platinum anodes are least acted upon and were generally used. The cathode reduction can be largely reduced by the addition of a little calcium hypochlorite to the electrolyte of potassium chloride. This forms a coating of lime on the cathode and increases the current efficiency greatly. The destruction of chlorates during electrolysis may also be reduced by maintaining the electrolyte slightly acid, either by the addition of a little hydrochloric acid, or of an acid salt such as potassium bichromate which probably forms a film of chromium oxide on the cathode and diminishes the hydrogen reduction. Copper cathodes are now generally used.

The process for the manufacture of potassium chlorate, which has been in very successful operation for a number of years, uses a solution of potassium chloride containing a little potassium bichromate, passing between anodes of platinum gauze, supported on a lead backing, and cathodes of copper in the shape of rods. The distance between the anodes and cathodes is only $\frac{1}{64}$ inch. The electrodes are kept apart by insulating knobs on the copper rods. The apparatus consists of rectangular wooden frames, alternating with lead plates which support the platinum gauze, packed together in a frame like a filter press, with rubber gaskets between. A great many cells thus occupy only a very small space, the current passing from one cell to the next in series. The rapid mixture of the primary anode and cathode products is brought about by the hydrogen bubbles formed at the cathode, and the rapid circulation of the electrolyte.

The chloride solution enters the apparatus at about 20° C., and leaves it at about 70° C. carrying about 3 per cent. of potassium chlorate. It passes to a refrigerator where the potassium chlorate crystallizes out, and after resaturation with potassium chloride and adjustment of the free-acid content it goes back into the process, the entire operation being continuous and practically automatic. The tempera-

ture of the cell is controlled by the rate of flow of the electrolyte. Owing to the much greater solubility of sodium chlorate, this process is not suitable for its production.

The purification of potassium chlorate, as produced by the various electrolytic modifications used, is confined exclusively to recrystallization from water. The crystals are usually drained and washed in a centrifugal machine and may be sold as coarse crystals; or they are ground to a fine powder in buhrstone mills, care being taken that no organic matter, dirt or metal such as iron, etc., gets into the mill, as an explosion would inevitably take place. Unusual precautions must be taken in such a mill to avoid disaster. No fire should be permitted in the building and heating should be confined to steam and all lighting should be electric. In addition, the grinding mill should be at a considerable distance from the main works.

AVAILABILITY OF SUPPLY.

What has been said about potassium chloride in the chapter on saltpeter may properly be said here, as all of the potassium chlorate manufactured is made from potassium chloride. The importation of potassium chlorate, given in Mineral Industry for 1917, is set forth in the following table:

Imports of potassium chlorate in tons of 2,000 pounds.

Year.	Quantity.	Value.
1913	618	$66,609
1914	20	3,408
1915	14	4,614
1916		
1917	218.7	193,738

According to an article which appeared in the Oil, Paint and Drug Reporter of March 24, 1919, the potassium-chlorate industry in Japan receives considerable attention. It seems that it was first made in that country in 1908, but it was not till 1912 that any considerable quantity appeared on the market. During the war the increase in prices stimulated the production very greatly, but overproduction, high freights, and shipping difficulties are now causing depres-

sion. The trade depends chiefly upon exports to the United States and to South America.

At the end of 1917 there were 49 factories engaged in the manufacture, the capital represented being 6,000,000 yen. The total capacity amounted to 10,000 tons a year, but the production was only 6,000 tons, 60 per cent. of which was made by three factories. The average domestic consumption of the product is about 3,700 tons.

Resources of potash in the United States (estimated possible yearly production).

125,000 tons from the iron industry
 72,000 tons from the cement industry
  2,000 tons from molasses
  2,000 tons from wood ashes
  4,000 tons from brines
  1,000 tons from kelp

Production of potassium chloride, in metric tons, in Germany.

Year.	Quantity.	Value.	Year.	Quantity.	Value.
1898	191,347	$6,380,220	1906	403,387	$11,034,632
1899	207,506	6,801,250	1907	473,138	12,639,704
1900	271,512	8,793,750	1908	511,258	13,369,174
1901	282,750	8,782,250	1909	624,994	16,245,642
1902	267,512	7,507,710	1910	741,259	17,371,144
1903	280,248	8,125,320	1911	838,420	19,851,342
1904	279,238	8,424,676	1912	506,744	16,336,792
1905	373,177	10,580,528			

USES OTHER THAN IN PYROTECHNICS.

Potassium chlorate is used in the manufacture of certain explosives such as cheddite, steelite, rack-a-rock, silesia, white gunpowder, and the like which have been mentioned. It is used in analysis and as an oxidizer in various chemical processes It has a limited use in medicine. Its use in railway fusees is now abandoned on account of its extreme sensitiveness.

PHYSICAL PROPERTIES.

Color and odor.—Commercial potassium chlorate is an almost white crystalline powder or lustrous tabular crystal of the monoclinic system. It has no odor.

Solubility.—One hundred cubic centimeters of water dissolve 3.3 grams at 0° C. and 60 grams at 104.8° C. This latter temperature is the boiling point of a saturated solution. It is insoluble in absolute alcohol.

Hygroscopicity.—The substance is not hygroscopic, and when not in contact with other materials, particularly organic matter, it does not alter on exposure to the air.

Flame color.—It imparts the usual violet color peculiar to potassium salts to the flame, with violent decrepitation.

Fusibility.—It melts at 357° C. and decomposes at 400° C. with a rapid evolution of oxygen. The heat of formation is 95,860 calories. It has a slightly bitter saline taste.

Hardness.—The crystals are soft and easily ground.

Specific gravity.—The specific gravity at 18° C. is 2.337.

CHEMICAL PROPERTIES.

GENERAL NATURE.

The molecular weight of potassium chlorate is 122.56. This is made up of potassium with an atomic weight of 39.1, chlorine with an atomic weight of 35.46, and three atoms of oxygen with a combined atomic weight of 48. It is the potassium salt of chloric acid and has the formula $KClO_3$. It does not carry water of crystallization.

REACTIONS.

The salt is neutral to litmus. It is soluble in pure nitric acid, but if NO_2 compounds are present it rapidly decomposes. Silver nitrate gives no precipitate. This easily distinguishes the salt from any soluble chlorides which are precipitated by silver nitrate. Sulphurous acid reduces potassium chlorate to potassium chloride; so does ferrous sulphate, as well as zinc and acetic acid. The decomposition of potassium chlorate by any of the above wet methods distinguishes it from soluble perchlorates and is the basis of the quantitative determination of the one in the presence of the other.

FUNCTIONS IN PYROTECHNIC PIECES.

Potassium chlorate plays a vital part in the pyrotechnic pieces in which it is used. Primarily, owing to the fact

that all of the oxygen content of the salt is easily available and is present in a concentrated condition, it acts as the consuming agent for the various combustible materials with which it is compounded. It is the most active of all the agents used for this purpose, and this activity imparts an element of danger, as it renders explosion and spontaneous combustion possible. Heat and friction are not the only agents which produce premature chemical actions in mixtures containing potassium chlorate. As it is the salt of a weak acid, easily replaced by other acids and extremely unstable in the free condition, any combination which contains free acid, or which may develop it by the continued close association of the materials existing in a state of compression, may also produce premature decomposition, thus making the compositions very dangerous to handle or store. This has been referred to in the historical introduction. From the standpoint of the large available oxygen content and the ease with which it is set free, the salt is ideal, but the element of danger is so great that its use is always attended with great hazard.

Although potassium salts impart their own characteristic violet color to the flame, the coloration is so delicate that it does not affect that produced by other compounds, such as salts of barium and strontium, whose flame colors are much more intense. At the present time we find that potassium chlorate is used in rocket red signal compositions, containing 66.6 per cent. strontium nitrate, 25 per cent. potassium chlorate, 8.4 per cent. orange shellac; in the Red Rifle light and Red Very light compositions containing potassium chlorate 72.7 per cent., strontium carbonate 15.2 per cent., orange shellac 12.1 per cent.; in Red Position lights containing potassium chlorate 37.5 per cent., strontium nitrate 50 per cent., orange shellac 12.5 per cent.; in Green Position lights containing barium chlorate 23.2 per cent., barium nitrate 59 per cent., potassium chlorate 6.3 per cent., orange shellac 10.5 per cent., stearin 1 per cent.; and in the Smoke Torch Blob containing potassium chlorate 88.9 per cent., red gum (gum Kauri) 7.4 per cent., charcoal (fine) 3.7 per cent.

METHODS OF ANALYSIS.

The following methods for the analysis of potassium chlorate are based on the assumption that the salt is the reasonably pure article known as commercial potassium chlorate.

QUALITATIVE TESTS.

Flame test.—This test shall be made in the ordinary manner by means of a platinum wire moistened with concentrated hydrochloric acid, dipped in the powdered salt and heated in the flame of a Bunsen burner. This test is made for the purpose of determining the purity of the salt in a general way, in order to indicate the method of procedure.

Sulphates.—Five grams of the potassium chlorate shall be dissolved in distilled water, and filtered if necessary. To the filtrate shall be added a solution of barium chloride. The formation of a white precipitate of barium sulphate indicates the presence of sulphates in the sample.

Chlorides.—To a moderately concentrated filtered solution of potassium chlorate shall be added a few drops of silver nitrate solution; the presence of chlorides in the sample will be indicated by the formation of a white precipitate of silver chloride. Turbidity in the solution will indicate the presence of traces only.

The following results were obtained from the qualitative tests made upon a sample of commercial potassium chlorate:

Flame test: Practically no sodium or calcium salts indicated.

Sulphates: Absent.

Chlorides: Traces only.

QUANTITATIVE TESTS.

Moisture.—A weighed sample of 3 grams shall be spread out on a 3-inch watch glass and dried in an air bath at 110° C. to constant weight. The loss in weight thus determined represents the amount of moisture present, and this loss in weight divided by the weight of the sample taken will give the percentage of moisture.

Potassium chlorate.—Eight-tenths gram of the sample shall be dissolved in distilled water and diluted to 500 c. c. in a

graduated flask. Fifty c. c. shall be drawn off with a pipette which has been standardized against the flask. This 50 c. c. portion shall be run into a 500 c. c. Erlenmeyer flask and diluted to about 150 c. c., whereupon 10 c. c. of 1:1 sulphuric acid shall be added. The contents of the flask shall now be heated almost to boiling, and 50 c. c. of a 4 per cent. solution of Mohr's salt, prepared by dissolving 10 grams of pure ferrous ammonium sulphate in previously boiled cold distilled water, and diluting to the mark in a 250 c. c. flask, shall be added. The flask shall be closed with a stopper carrying a Bunsen valve, and the solution boiled two minutes. The valve shall now be removed, the solution cooled, and the excess of Mohr's salt titrated immediately with approximately one-tenth-normal $KMnO_4$ solution.

The oxidation of the Mohr's salt by potassium permanganate proceeds according to the reaction $10[NH_4)_2SO_4$. $Fe SO_4.6 H_2O]+2 KMnO_4+8 H_2SO_4=10 (NH_4)_2SO_4+5 Fe_2$ $SO_4)_3+K_2SO_4+2MnSO_4+68H_2O$. In this reaction 10 molecules of Mohr's salt are equivalent to 2 molecules of potassium permanganate. Now, in acid solution the available oxygen of potassium permanganate is liberated according to the reaction $2 KMnO_4+3 H_2SO_4=K_2SO_4+2 MnSO_4+5 O+3 H_2O$. From the first reaction above we see that 10 molecules of the Mohr's salt are equivalent to 2 molecules of potassium permanganate, which in turn are equivalent to 5 atoms of oxygen; consequently 2 molecules of Mohr's salt are equivalent to 1 atom of oxygen. Mohr's salt has the molecular weight of 392.14; consequently the atomic weight of oxygen 16, divided by twice 392.14, or 784.28, will give the factor by which it is necessary to multiply any given weight of Mohr's salt in order to obtain the amount of oxygen required to oxidize it. This factor is 0.02041.

In standardizing the potassium permanganate solution 50 c. c. of the Mohr's-salt solution, containing two grams of the substance, are titrated with the potassium permanganate as above indicated. The weight of the Mohr's salt used, multiplied by the factor 0.02041, and divided by the number of cubic centimeters of the permanganate solution required for the titration, will give the available oxygen content of 1 c. c. of the potassium-permanganate solution. Further, the vol-

ume of the potassium-permanganate solution which is equiv-
alent to 1 c. c. of the Mohr's-salt solution shall be noted.

With the potassium chlorate and sulphuric acid, Mohr's
salt reacts as follows $6(NH_4)_2SO_4.FeSO_4.6H_2O+KClO_3+$
$3H_2SO_4=6(NH_4)_2SO_4+3Fe_2(SO_4)_3+KCl+39H_2O$.

After determining the volume of potassium permangan-
ate required for the Mohr's salt which has not been oxidized
by the potassium chlorate, the equivalent volume of the
Mohr's salt solution shall be figured. This gives the volume
of the Mohr's salt solution which was present in excess of
that required by the potassium chlorate. Deducting this
from the total volume of Mohr's salt solution used gives the
volume consumed by the potassium chlorate, and this volume
multiplied by the weight of Mohr's salt contained in each
cubic centimeter gives the weight of Mohr's salt consumed
by the potassium chlorate. This weight multiplied by the
factor 0.02041 gives the oxygen content of the potassium
chlorate. The molecular weight of potassium chlorate is
122.56, and it contains three atoms of oxygen with a total
atomic weight of 48, consequently, the weight of the oxygen
content, multiplied by the fraction $\frac{122.56}{48}$ or 2.553 will give
the weight of potassium chlorate in the sample used, and
this weight divided by the weight of the sample will give
the percentage of potassium chlorate.

Hypochlorites.—Five grams of the sample shall be dis-
solved in 100 c. c. of cool distilled water, and potassium-
iodide starch solution in excess shall be added, together with
about one gram of sodium bicarbonate. The presence of hy-
pochlorites is indicated by the immediate appearance of a
blue coloration. If the presence of hypochlorites is indi-
cated, they shall be determined in the following manner,
which depends upon the reaction, $KClO+2KI+H_2O=$
$KCl+2I+2KOH$. The function of the sodium bicarbonate
is to combine with the KOH liberated. The amount of iodine
liberated is then determined by titrating with a one-tenth-
normal solution of sodium arsenite, which is oxidized by the
iodine to sodium arsenate, Na_3AsO_4, according to the reac-
tion $Na_3AsO_3+2I+H_2O=Na_3AsO_4+2HI$. As this last re-
action is reversible and may be made to go quantitatively in

either direction by varying the conditions, it is necssary to have a compound present which shall combine with the hydriodic acid, as fast as it is liberated. Free alkali may not be used for this purpose as it reacts with free iodine, forming a mixture containing iodide, hypoiodite and iodate; sodium bicarbonate, $NaHCO_3$, has been found to be the best adapted for this purpose, and consequently its use is recommended in the procedure.

In performing the operation, it is necessary to have a one-tenth-normal solution of sodium arsenite as a standard. This is prepared from commercial vitreous white oxide of arsenic, As_2O_3. If the commercial arsenic contains the sulphide, it shall be freed from it, by dissolving in hot 1.2 hydrochloric acid and filtering, the sulphide of arsenic being insoluble under these conditions. On cooling, As_2O_3 will crystallize out. The crystals are thoroughly washed with water, dried in an air bath and sublimed from a porcelain dish onto a watch glass. The sublimate is allowed to stand in a desiccator over calcium chloride for 12 hours. As the molecular weight of As_2O_3 is 197.92, 4.95 grams of the As_2O_3 are required for one liter of one-tenth-normal sodium arsenite. This amount is therefore weighed out, placed in a porcelain dish, and dissolved by warming with a small amount of a concentrated solution of caustic soda. This requires three or four minutes. The solution is transferred to a liter flask, diluted to about 400 c. c. and a drop of phenolphthalein solution added. Dilute sulphuric acid shall then be added until the red color vanishes. A filtered solution, containing 20 grams of sodium bicarbonate in 500 c. c. of water, shall then be added. If the solution now reacts alkaline to the phenolphthalein, dilute sulphuric acid shall again be added until it is decolorized. Finally the solution shall be made up to a volume of 1,000 c. c.

Procedure.—To the solution of 5 grams of the sample being examined in 100 c. c. of cold water, one gram of pure sodium bicarbonate shall be added. An excess of a 10 per cent. solution of potassium iodide containing starch shall be now added, and the solution shall then be titrated with the one-tenth-normal soluton of sodium arsenite described above, until the blue color just vanishes. From the reactions, it is evident that one molecule of sodium arsenite is equivalent

to two atoms of iodine, which in turn are equivalent to one molecule of potassium hypochlorite. As each cubic centimeter of the sodium-arsenite solution contains 0.00495 gram As_2O_3, each cubic centimeter of sodium-arsenite solution is equivalent to 0.00453 grams KClO, this being the KClO content of 1 c. c. of a one-tenth-normal solution, as the molecular weight of KClO is 90.56. Consequently, the volume of the sodium-arsenite solution consumed, multiplied by 0.00453, will give the weight of potassium hypochlorite in the sample taken, and this amount divided by the weight of the sample will give the percentage of the potassium-hypochlorite content.

Bromates.—In making this determination, the following solutions are required:

(*a*) Approximate normal hydrochloric acid, containing 36.5 grams HCl in 1,000 c. c. This solution may be prepared with sufficient accuracy by diluting 100 c. c. of the concentrated hydrochloric acid with 900 c. c. of water.

(*b*) A 10 per cent. solution of potassium iodide containing starch, made by dissolving 10 grams of potassium iodide in 100 c. c. of water and adding a little starch paste.

(*c*) Approximately one-tenth-normal solution of sodium thiosulphate.

In making this determination the bromates react in the presence of hydrochloric acid with potassium iodide, liberating iodine according to the reaction.

$$KBrO_3 + 6KI + 6HCl = KBr + 6KCl + 3H_2O + 6I \text{ and}$$
$$2Na_2S_2O_3 + 2I = 2NaI + Na_2S_4O_6.$$
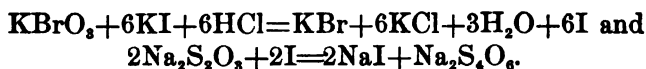
In order to prepare and standardize the solution of sodium thiosulphate, 25 grams of the salt shall be dissolved in 1,000 c. c. of water. This will give a solution of approximately one-tenth-normal strength. It is standardized by the use of a solution of pure iodine in potassium iodide which is free from iodate. The iodine shall be prepared by grinding the commercial article with potassium iodide and subliming the mixture. The iodine thus obtained shall be resublimed and will then be of sufficient purity for use.

In a small weighing bottle with a tight-fitting glass stopper, about 2 grams of potassium iodide shall be placed to-

gether with about 0.5 c. c. of water which will dissolve the iodide. After wiping the neck of the bottle and the stopper free from any adhering liquid, the bottle shall be closed and carefully weighed. After the weight is noted, from 0.4 to 0.5 gram of the resublimed iodine shall be introduced, the bottle closed with the stopper and immediately weighed, the difference in the weights being the amount of iodine added. It will be found that this amount of iodine will dissolve readily in the potassium-iodide solution. The bottle shall then be dropped into a 500 c. c. Erlenmeyer flask containing 200 c. c. of water and 1 gram of KI; the stopper shall be removed from the bottle just as it is dropped and shall be allowed to follow the bottle into the flask. The solution of sodium thiosulphate to be standardized shall then be run in from a burette until the iodine color has almost disappeared, a small amount of starch solution shall then be added, and the addition of the sodium-thiosulphate solution continued until the blue color just vanishes. This will give the volume of the thiosulphate solution, which is equivalent to the weight of iodine used, from which the iodine equivalent of 1 c. c. of the thiosulphate solution shall be calculated.

From the equation, it is evident that 1 molecule of potassium bromate is equivalent to 6 atoms of iodine, or, as the bromate content of the sample analyzed is to be reported in terms of bromine, 1 atom of bromine is equivalent to 6 atoms of iodine. These 6 atoms of iodine have the combined atomic weight of 761.52, while bromine has the atomic weight of 79.92; consequently the iodine equivalent of 1 c. c. of the thiosulphate solution as above determined, multiplied by the fraction $\frac{79.92}{761.52}$ or 0.10495, will give the bromine equivalent of 1 c. c. of the thiosulphate solution when the bromine is present as potassium bromate.

Procedure: Two grams of the sample shall be dissolved in 100 c. c. of distilled water, 5 c. c. of the normal hydrochloric acid, and 5 c. c. of the 10 per cent. solution of potassium iodide, with a little starch paste, shall be added and the mixture allowed to stand for an hour in a dark place. The blue coloration, due to the action of the potassium bromate on the potassium iodide in connection with the starch, will be found to increase in density on standing. The solution shall then be titrated with the standard sodium-thiosulphate

solution until the blue coloration just disappears. The volume of the thiosulphate solution required, multiplied by its bromine equivalent per cubic centimeter, will give the bromine content of the sample, and this divided by the weight taken will give the percentage of the bromine content of the sample which is present in the form of bromates.

Acidity.—Five grams of the sample shall be dissolved in 100 c. c. of previously boiled distilled water. Delicate neutral litmus paper shall show no acid reaction after 15 minutes immersion.

Insoluble matter.—A weighed sample of about 10 grams shall be dissolved in about 200 c. c. of warm water and the solution filtered through a weighed Gooch crucible, the residue thoroughly washed, dried at 110°, and weighed. This weight divided by the weight of the sample taken will give the percentage of insoluble matter.

Calcium salts.—Five grams of the sample shall be dissolved in 100 c. c. of distilled water and boiled with 20 c. c. of concentrated hydrochloric acid. The solution shall be then filtered if necessary, made alkaline with ammonia, and an excess of ammonium oxalate, added. The solution carrying the precipitate of calcium oxalate shall be boiled for 4 minutes and allowed to stand several hours before filtering. If very small amounts of calcium are present, it is preferable to allow the solution to stand over-night. The precipitate of calcium oxalate shall then be filtered and thoroughly washed. The filter paper is removed from the funnel, opened up and placed on the inside of a 400 c. c. beaker, to which shall then be aded 300 c. c. of water containing 20 c. c. of sulphuric acid. The solution shall then be heated to 70° C. and titrated with one-tenth-normal $KMnO_4$.

After the potassium chlorate has been boiled with hydrochloric acid, any calcium salts will be present as calcium chloride, $CaCl_2$. After the acid solution has been made alkaline with the ammonia, it will contain both ammonia in excess and ammonium chloride. This will prevent the precipitation of any magnesium salts which may be present, and the ammonia and ammonium chloride will have no effect upon the calcium chloride. The ammonium oxalate acts upon the calcium chloride, forming calcium oxalate according to the reaction $CaCl_2 + (NH_4)_2C_2O_4 = CaC_2O_4 + 2NH_4Cl$. The calcium oxalate when treated with potassium perman-

ganate in the presence of sulphuric acid, is oxidized according to the equation—

$$5CaC_2O_4 + 2KMnO_4 + 8H_2SO_4 =$$
$$5CaSO_4 + 10CO_2 + K_2SO_4 + 2MnSO_4 + 8H_2O$$

As has already been shown, $2KMnO_4$ is equivalent to 5 atoms of available oxygen under acid conditions; consequently, 1 molecule of CaC_2O_4 is equivalent to 1 atom of oxygen. It is also evident that 1 molecule of CaC_2O_4 is equivalent to 1 molecule of CaO in terms of which the calcium salts contained in the sample are to be reported. It follows, therefore, that the molecular weight of CaO, 56.07, divided by the atomic weight of oxygen, 16, will give the factor needed by which to multiply the available oxygen content of the potassium permanganate used for the titration, to obtain the CaO content. This factor is 3.5043. The weight of CaO thus obtained, divided by the weight of the sample taken, will give the percentage of CaO.

Sodium salts.—The amount of sodium salts shall be determined in the following manner:

One gram of the potassium chlorate shall be treated with 10 c. c. of water and 5 c. c. of concentrated nitric acid. The salt shall then be evaporated to dryness and the residue dissolved in a little hot water. A drop of the solution shall then be removed on the end of a stirring rod and added to a solution of silver nitrate which has been rendered slightly acid with nitric acid. If chlorides are present, it will be indicated by the formation of a precipitate of silver chloride. The evaporation with nitric acid shall be continued until the chlorides are entirely converted into nitrates. When this has been accomplished, the solution shall be evaporated to dryness to remove the excess of nitric acid, and the sodium determination shall be made in accordance with the method outlined in the chapter on potassium nitrate.

The following results were obtained from the quantitative tests made upon the above sample:

Moisture:

	Grams.
Weight taken	3
Weight after drying	2. 9982
Loss in weight	. 0018

This gives 0.06 per cent.

Potassium chlorate:

	Grams.
Weight taken _____	0. 08
Number of cubic centimeters of potassium permanganate used _____	12. 2
Number of cubic centimeters of potassium permanganate used for 50 cubic centimeters of Mohr's salt____	51. 2

One cubic centimeter KMnO$_4$ solution thus equals 0.98 c. c. of the Mohr's salt solution. Therefore, the volume of potassium-permanganate solution consumed equals 39 c. c. = 38.22 c. c. Mohr's salt solution=1.5288 grams of Mohr's salt. This, when multiplied by the factor 0.02041, gives 0.0312 gram as the oxygen content of the KClO$_3$ used. This, multiplied by the factor 2.553, gives 0.0797 gram as the KClO$_3$ content. The weight of the sample in the 50 c. c. used=0.080 gram, and the weight obtained, 0.0797 gram, divided by this gives 99.6 per cent. as the percentage of KClO$_3$ in the sample.

Hypochlorites: Absent.

Bromates:

	Grams.
Weight taken_____ _____	2
1 c. c. Na$_2$S$_2$O$_3$ solution used=_____	. 012685
Number of cubic centimeters of Na$_2$S$_2$O$_3$ used_____	1. 4
I equivalent of Na$_2$S$_2$O$_3$ used=_____	. 0178

This, multiplied by the factor 0.10495 gives 0.0019 gram; divided by the weight taken, gives 0.095 per cent. bromine present as bromate.

Acidity: None.

Insoluble matter: A trace only.

Calcium salts: Absent.

The above results are tabulated as follows:

Moisture _____	0. 06
Potassium chlorate _____ _____	99. 60
Bromine_____	. 09

SPECIFICATIONS.

The results of the research work and the investigation of the manufacture of potassium chlorate make it desirable that the following specifications be adopted for use in Military Pyrotechnics:

1. The material shall be white or at least show only a slight yellowish tinge.
2. The material shall be odorless.

---

¹ Gram I.

3. The material shall contain not less than 99.5 per cent. of $KClO_3$.
4. The material shall contain no hypochlorites.
5. The material shall contain not more than 0.1 per cent. bromates calculated as bromine.
6. The material shall contain not more than 0.25 per cent. of sodium salts, calculated as the oxide.
7. The material shall contain not more than 0.25 per cent. of calcium salts, calculated as the oxide.
8. When compounded it shall contain not more than 0.2 per cent. of moisture.
9. The material shall contain no organic or oxidizable substances.
10. When compounded the material shall be ground so that all will pass through an 80-mesh sieve and 60 per cent. will pass through a 100-mesh sieve.

DISCUSSION OF SPECIFICATIONS.

The purity of commercial potassium chlorate is very high, and it is advisable to make the specifications exclude material which may have been prepared in a careless manner. The limitations set upon the percentage of sodium salts and calcium salts are based upon the fact that the flame color becomes seriously impaired for pyrotechnic use when appreciable quantities of these salts are present.

Some manufacturers claim that the presence of moisture in mixtures containing potassium chlorate, in connection with the various reducing materials used in pyrotechnic pieces, has a tendency to produce free acid within the composition itself, particularly when it exists in the state of compression, in which it occurs in the finished pieces. The development of any small amount of acid would create a "zone of unrest" within the composition which would add greatly to the danger of handling and storing the finished pieces. On this account the percentage of moisture in the potassium chlorate itself, and in all the substances compounded with it as well, should be as low as possible.

CHAPTER X.

BARIUM CHLORATE.

HISTORY.

Barium chlorate was first prepared after barium chloride and sodium chlorate were known, as it was made originally from solutions of these two substances. The combined solutions were concentrated, and as sodium chloride is more insoluble than barium chlorate, it separated out first. On continued evaporations, barium chlorate crystallized out and was purified by recrystallization. It was also prepared, subsequent to this, by suspending barium carbonate in boiling water and passing chlorine gas through the solution. The barium chlorate was subsequently crystallized from this liquid.

OCCURRENCE IN NATURE.

Barium chlorate does not occur in nature and occupies no position of any kind in mineralogy.

METHOD OF MANUFACTURE.

The method of manufacture of barium chlorate necessarily involves the preparation of barium chloride, from which it is invariably derived. Barium chloride, carrying 2 molecules of water of crystallization and known as Terra Ponderosa Salita, may be prepared either from witherite, the native carbonate of barium, or heavy spar, the native sulphate of barium. The witherite is dissolved in dilute hydrochloric acid and then allowed to stand for some time with an excess of the carbonate, in order to precipitate iron and other foreign metals present in the mineral; barium hydrate in solution, sometimes called baryta water, somewhat increases the rapidity of this reaction. The solution from this acid and carbonate treatment is filtered, the filtrate neutralized

151

with hydrochloric acid, and the salt, barium chloride, is crystallized out by evaporation and purified by recrystallization.

When barium chloride is prepared from the native sulphate either of two methods may be used. In the first method, the barium sulphate is heated in a large crucible with powdered coal when decomposition sets in and the barium sulphate is reduced to barium sulphide. The mass is then lixiviated and the aqueous solution is treated with hydrochloric acid, whereby barium chloride is formed according to the reaction, $BaS + 2HCl = BaCl_2 + H_2S$. An excess of hydrochloric acid is added and the liquid is boiled until it is freed from sulphureted hydrogen; it is then allowed to cool and the barium chloride is crystallized out by evaporation.

The alternative method for the preparation of barium chloride from the native barium sulphate consists in heating together 100 parts of finely powdered heavy spar, 40 parts of charcoal, 20 parts of limestone, and 50 parts of calcium chloride. This is done in a reverberatory furnace at a red heat; the resultant reaction from this ignition produces barium chloride and calcium sulphide. The mass is then lixiviated with water, whereby barium chloride goes into solution, leaving the insoluble calcium oxysulphide, formed by the union of the sulphide with the oxide of calcium produced by the ignition of the limestone.

In this process, manganese chloride, left as a by-product of the chlorine manufacture, may be used in place of calcium chloride, a little sand being added along with the limestone or chalk. The mass is heated on a cast-iron plate.

Commercial barium chloride generally contains small quantities of strontium and calcium chlorides, together with traces of chlorides of iron, aluminum, copper, and lead. Washing the crystals with alcohol removes both the strontium and calcium chlorides, while calcium chloride may also be removed by digesting with barium carbonate suspended in water, whereby the calcium chloride becomes converted to the carbonate, or more rapidly by adding baryta water and passing CO_2 into the liquid. The digestion with barium carbonate also precipitates the sesquioxides of iron and aluminum. Lead and copper are best removed by the addition of a little barium sulphide.

Barium chloride may be recovered from mixtures of the chlorides of the alkalies and alkaline earths by treating the concentrated liquor with a hot saturated solution of sodium chloride, whereby, on cooling, a mixture of barium and sodium chlorides crystallizes out; by treating a cold saturated solution of this mixture with twice its volume of hydrochloric acid barium chloride is precipitated.

The barium chlorate of commerce is invariably prepared by the electrolysis of barium chloride, according to the detailed scheme of manufacture outlined in the chapter on potassium chlorate. The crystallization of the barium chlorate from the electrolyte in these processes is more difficult to attain on account of its greater solubility. The conditions for its crystallization are similar to those of sodium chlorate.

AVAILABILITY OF SUPPLY.

As the barium chlorate of commerce is invariably prepared from barium chloride, which itself is prepared from the minerals barite and witherite, a consideration of these compounds will furnish the necessary data regarding the availability of the supply of barium chlorate. The barium industries are marked by rapid expansion, and the growth since 1914, although started by the war to replace the products formerly imported, will not be adequte in a short time to supply our domestic demands. In 1917 there were being produced in the United States barium products four and one-quarter times the value of the importations of 1914.

This great increase is due in part to high prices, but more largely to increased use of the different barium compounds. Some of this increase is due to the general expansion of business, but not a little to the superiority of domestic goods which permits their use, where formerly the imported goods were not satisfactory. An example of this is the use of the domestic precipitated barium sulphate in the rubber industry.

According to Mineral Industry for 1917, the American barium industry can now produce an adequte supply of high-quality products, owing to the expansion which has been made in the last three years, but from present indications it will have to be duplicated in the coming three years.

The increase in production of barytes, as shown by the following tables, gives a good idea of the rapid expansion of the barium industry in the United States.

Marketed production of crude barytes in the United States.

Year.	Short tons.	Year.	Short tons.	Year.	Short tons.	Year.	Short tons.
1900.........	67,680	1905.........	48,235	1910.........	42,975	1915.........	108,547
1901.........	49,070	1906.........	50,231	1911.........	38,445	1916.........	221,952
1902.........	61,668	1907.........	89,621	1912.........	37,478		
1903.........	50,397	1908.........	38,527	1913.........	45,298		
1904.........	65,727	1909.........	61,945	1914.........	52,747		

Crude barytes marketed in the United States.

State.	1914			1915			1916		
	Quantity (short tons).	Value.	Average price per ton.	Quantity (short tons).	Value.	Average price per ton.	Quantity (short tons).	Value.	Average price per ton.
Alabama.............	(¹)	(¹)	....	(¹)	(¹)	....	7,631	$27,198	$3.56
Colorado............							481	3,005	6.25
Georgia.............	(¹)	(¹)	....	31,027	$102,825	$3.31	104,784	401,295	3.83
Kentucky...........	(¹)	(¹)	....	7,753	28,427	3.67	11,068	54,995	4.97
Missouri	33,317	$112,231	$3.37	39,113	158,597	4.05	58,223	365,111	6.27
North Carolina......	(¹)	(¹)	....	(¹)	(¹)	....	878	3,246	3.70
Tennessee...........	10,113	16,273	1.61	25,074	71,390	2.85	32,416	123,986	3.85
Other States ².......	9,317	27,143	2.91	5,580	19,793	3.55	6,471	32,396	5.01
	52,747	155,647	2.95	108,547	381,032	3.51	221,952	1,011,232	4.56

¹ Included in "Other States."
² Includes, 1914: Alabama, California, Georgia, Kentucky, North Carolina, South Carolina, and Virginia. 1915: Alabama, Alaska, California, North Carolina, South Carolina, and Virginia. 1916: California, Nevada, South Carolina, and Virginia.

Crude barytes imported for consumption.

Year.	Quantity (short tons).	Value.	Year.	Quantity (short tons).	Value.
1912.....................	26,186	$52,467	1915.....................	2,504	$4,877
1913.....................	35,840	61,409	1916.....................	17	245
1914.....................	24,423	46,782	1917.....................	5	63

Apparent consumption of crude barytes (short tons).

Year.	Sales of domestic barytes.	Imports for consumption.	Apparent consumption.	Year.	Sales of domestic barytes.	Imports for consumption.	Apparent consumption.
1911.........	38,445	20,214	58,659	1914.........	52,747	24,423	77,170
1912.........	37,478	26,186	63,664	1915.........	108,547	2,504	111,051
1913.........	45,298	35,840	81,138	1916.........	221,952	17	221,969

Crude barytes used in the manufacture of barium products (short tons).

Year.	For barium chemicals.	For ground barytes.	For lithopone.	Total.
1915...	10,216	53,903	44,503	108,622
1916...	38,283	75,507	71,898	185,688

The production in Tennessee, in 1917, was 36,839 short tons; in Georgia, 115,434 tons; in Wisconsin, 64,997 tons. The total production in the United States during 1917 should reach 300,000 tons.

The Thomson Weiman Co., operating mostly in Georgia, with minor operations in Kentucky, reported 56,500 short tons as their production in 1917.

Witherite (crude barium carbonate).—No workable deposits of this mineral are as yet developed in the United States. A deposit of workable quantity and quality is reported near El Portal, Mariposa County, Calif.

Imports of barium products, fiscal year, ending June 30.

	1915		1916		1917	
	Quantity.	Value.	Quantity.	Value.	Quantity.	Value.
Baryta, sulphate of, or barytes, including baryta earth; unmanufactured, long tons.......	9,616	$21,087	15	$245	....	....
Manufactured, long tons.........	1,755	14,997	....	....	210	$3,813
Blanc fixe, or artificial sulphate, of barytes, and satin white, or artificial sulphate of lime, pounds.....................	2,233,369	25,748	492,723	11,523	408,163	10,029
Lithopone, pounds...............	6,205,245	195,828	5,122,083	414,573	231,869	20,591
Barium carbonate, pounds.......	844,588	7,864	6	2	804	177
Barium binoxide, pounds.........	4,084,588	311,262	546,442	48,451	....	....
Barium chloride, pounds.........	4,686,029	60,532	50	10	6,614	608

Barium products of domestic manufacture sold.

Chemical.	1915, quantity (short tons).[1]	1916		
		Quantity (short tons).	Value.	Average price per ton.
Barium binoxide................................	(²)	1,980	$1,089,923	$550.47
Barium carbonate................................	2,746	6,844	343,582	50.20
Barium chloride................................	2,106	3,643	238,490	65.46
Barium nitrate................................	971	446	97,881	219.46
Barium sulphate (blanc fixe)...................	(²)	3,337	167,404	50.17
Other barium chemicals ³......................	3,000	542	25,250	46.59
	8,823	16,792	1,962,520	116.87
Ground barytes................................	51,557	65,440	964,802	14.74
Lithopone....................................	46,494	51,291	5,798,927	113.06
	106,874	133,523	8,726,249	65.35

[1] Value of production in 1915 not available for publication.
² Included with "Other barium chemicals."
³ Includes, 1915, binoxide, hydroxide, sulphate, sulphide, and other barium chemicals not specified; 1916, hydroxide and sulphide.

BARIUM PRODUCTS.

Blanc fixe and precipitated barium sulphate.—The production for 1917 was approximately 8,000 tons, valued at $400,000, the greater part of which was consumed by the rubber, paint, and paper trades.

Precipitated barium carbonate.—The production for 1917 was approximately 2,500 tons, valued at $150,000, the greater part of which was consumed by the glass, ceramic, and chemical trades.

Barium chloride.—The production for 1917 was approximately 6,000 tons, valued at $420,000, the greater part of which was consumed by the chemical, color, and leather trades.

Barium nitrate.—The production of 1917 was approximately 4,000 tons, valued at $960,000, the greater part of this was consumed by the chemical and explosive trades.

Barium dioxide or peroxide.—The production for 1917 was approximately 2,500 tons, valued at $1,375,000, the greater part of which was consumed by manufacturers of hydrogen peroxide. A small quantity was used by the munition trade and some in the arts as an oxidizing agent.

The total value of the approximated production of barium products, not including lithopone, for 1917 was $3,305,000.

In the manufacture of the above barium products, barytes is the sole source of supply for raw material. The starting point of most manufacturing processes is to reduce the barytes to barium sulphide by mixing it with coal and heating it in a rotary furnace. In some cases, the sulphide thus made is heated directly to incipient fusion with calcium chloride to make barium chloride.

Barium sulphate is generally made by precipitating it from barium-sulphide solution with sodium sulphate.

Barium carbonate is made correspondingly, by precipitating it from the sulphide with sodium carbonate.

Barium nitrate is made from barium chloride and sodium nitrate.

Barium dioxide is made from barium nitrate by heating it to form the oxide and then oxidizing the oxide to the peroxide.

Statistics of barytes in the principal countries (metric tons).

	1912	1913	1914	1915	1916
Austria-Hungary (exports):			•		
Barium chloride................	3,659	4,918	....	....	....
Barytes........................	2,690	753	....	....	....
Belgium (production)..................	32,400	12,000	....	....	....
Canada (production)..................	421	582	555	499	1,241
France (production)...................	13,620	12,236	....	....	....
Baden (production)...................	15,871	16,445	....	....	....
Bavaria (production)..................	27,199	27,199	....	....	....
Germany (exports):					
Barytes.......................	142,681	158,065	....	....	....
Barium, white.................	8,242	7,647	....	....	....
Barium chloride...............	8,096	5,649	....	....	....
Brytes (imports)..............	18,666	19,466	....	....	....
Italy (production):					
Barytes, crude................	13,420	12,970	12,970	17,850	16,903
Barytes (imports).............	1,986	1,771	1,409	1,319	1,398
Barytes (exports).............	381	234	210	3,288	2,755
Spain (production)...................	1,096	3,049	....	4,218	10,506
Sweden (imports)....................	644	610	730	1,665	......
United Kingdom (production)..........	43,453	48,792	49,718	63,483	77,258
United States (imports)..............	27,093	37,490	26,025	3,460	149
United States (production)............	34,009	41,105	47,865	98,500	202,855

USES OTHER THAN IN PYROTECHNICS.

Barium chlorate has very little use either in the arts or sciences other than in pyrotechnic compositions. Like other soluble barium salts, it is very poisonous. Its use in dyeing is limited.

PHYSICAL PROPERTIES.

Color and odor.—The commercial barium chlorate is a white crystalline powder, or white transparent crystals of the monoclinic system, and is without odor.

Solubility.—100 c. c. of water will dissolve 19.2 grams at 3° C. and 111.2 grams at 100° C. It is slightly soluble in 95 per cent. alcohol and the alcoholic solution burns with a green flame.

Hygroscopicity.—The substance is not hygroscopic and does not alter on exposure to the air.

Flame color.—It imparts the usual green color to the flame, which is characteristic of barium salts. It does so with violent decrepitation.

Fusibility.—On heating, barium chlorate decomposes, giving off all of its oxygen content and leaving barium chloride behind. The melting point of the anhydrous salt is 414° C.

Taste.—It has an unpleasant, bitter, sharply saline taste, exciting nausea.

Hardness.—It is a soft compound and easily ground.

Specific gravity.—The specific gravity is 3.179 at 18° C.

CHEMICAL PROPERTIES.

GENERAL NATURE.

The molecular weight of barium chlorate is 322.306. This is made up of barium with an atomic weight of 137.37, 2 atoms of chlorine with a combined atomic weight of 70.92, and 6 atoms of oxygen with a combined atomic weight of 96, and 1 molecule of water with a molecular weight of 18.016. It is the barium salt of chloric acid, and has the formula $Ba(ClO_3)_2,H_2O$, and carries, as indicated in the formula, 1 molecule of water of crystallization.

REACTIONS.

The salt is neutral to litmus. When fused and plunged into a jar of coal gas, it gives up all of its oxygen content and burns with a brilliant illumination. Silver nitrate gives no precipitate. Sulphurous acid, ferrous sulphate, zinc, and acetic acid reduce barium chlorate to barium chloride. The reactions of the salt are similar to those of potassium chlorate, particularly so far as the ClO_3 content is concerned.

FUNCTIONS IN PYROTECHNIC PIECES.

Like potassium chlorate, barium chlorate plays two parts in the pyrotechnic compositions in which it is included. First, it supplies the oxygen required for the combustion, and second, it gives to the flame the characteristic green color of barium compounds. At the present time, barium chlorate is used in three compositions; the rocket green signal composition, consisting of barium chlorate 55.5 per cent., barium nitrate 33.3 per cent. and orange shellac 11.2 per cent.; the green rifle light and green Véry light compositions, which consist of barium chlorate 90 per cent., orange shellac 10 per cent.; the green position light composition containing barium chlorate 23.2 per cent., barium nitrate 59 per cent., potassium chlorate 6.3 per cent., orange shellac 10.5 per cent., stearin 1 per cent.

Like other chlorates, the use of the barium compound may be regarded as dangerous in handling, transportation and storage. Compared with potassium chlorate, the fact that the barium compound contains 1 molecule of water of crystallization may render it more dangerous for storage, as it seems to be the consensus of opinion among pyrotechnic manufacturers that the presence of water tends to produce a condition of unstable chemical equilibrium. On the other hand, barium chlorate does not melt or decompose at as low a temperature as potassium chlorate, and this may contribute a compensating factor of safety. Barium chlorate loses its water of crystallization at a low temperature, and it might be possible to use the anhydrous salt, thus avoiding any danger which the water of crystallization might induce. It should be noted also that, while the percentage of available oxygen in anhydrous barium chlorate is not as great as in potassium chlorate, the ratio being as 31.55 to 39.16, still its use, other things being equal, might be advantageous on account of its higher temperature of decomposition and its greater specific gravity.

METHODS OF ANALYSIS.

The following methods for the analysis of barium chlorate are based on the assumption that the salt is the reasonably pure article, known as commercial barium chlorate.

QUALITATIVE TESTS.

Flame test.—This test shall be made in the ordinary manner, by means of a platinum wire moistened with concentrated hydrochloric acid, dipped in the powdered salt, and heated in the flame of a Bunsen burner. This test is made for the purpose of determining the purity of the salt in a general way, in order to indicate the method of procedure.

Chlorides.—To a moderately concentrated filtered solution of barium chlorate shall be added a few drops of silver-nitrate solution. The presence of chlorides in the sample will be indicated by the formation of a white precipitate of silver chloride. Turbidity in the solution will indicate the presence of traces only.

The following results were obtained from the qualitative tests made upon a sample of commercial barium chlorate:

Flame test.—No sodium or calcium salts were indicated.

Chlorides.—Traces only.

QUANTITATIVE TESTS.

Moisture.—A weighed sample of three grams shall be spread out on a 3-inch watch glass and dried in an air bath at 110° C. to constant weight. The loss in weight thus determined represents the amount of moisture present, and this loss divided by the weight taken will give the percentage of moisture in the sample. The drying of the salt above this temperature should be avoided, as there will be danger of loss, due to the driving off of the water of crystallization, which is contained in the salt.

Barium chlorate.—Eight-tenth gram of the sample shall be dissolved in distilled water and diluted to 500 c. c. in a graduated flask. Fifty cubic centimeters shall be drawn off with a pipette, which has been standardized against the flask, and run into a 500 c. c. Erlemeyer flask, and diluted to about 150 c. c., whereupon 10 c. c. of 1:1 sulphuric acid shall be added. The contents of the flask shall be heated almost to boiling; 50 c. c. of a 4 per cent. solution of Mohr's salt, ferrous ammonium sulphate, shall be added, the flask closed with a stopper carrying a Bunsen valve and the solution boiled two minutes. The Mohr's salt shall be prepared in the manner outlined in the determination of potassium chlorate,

in the chapter on that compound. The valve shall be removed, the solution cooled, and the excess of Mohr's salt titrated immediately with approximately one-tenth-normal $KMnO_4$. The oxidation of the Mohr's salt by the potassium permanganate, as well as the calculations, are similar to those given in detail in the chapter on potassium chlorate. The molecular weight of barium chlorate is 322.306, and it contains 6 atoms of oxygen, with a total atomic weight of 96, consequently the weight of available oxygen as determined by the titration, multiplied by the fraction $\frac{322.306}{96}$ or 3.357, will give the weight of barium chlorate in the sample used, and this weight, divided by the weight taken, will give the percentage of barium chlorate.

Hypochlorites.—Five grams of the sample shall be dissolved in 100 c. c. of cold distilled water and 5 c. c. of potassium-iodide starch solution shall be added, together with about 1 gram of sodium bicarbonate. The presence of hypochlorites is indicated by the immediate appearance of a blue coloration in the solution. If the presence of hypochlorites is indicated, they shall be determined as described in the paragraph on hypochlorites in the chapter on potassium chlorate. The reactions involved are similar to those found with potassium chlorate.

Bromates.—The procedure in the determination of bromates is similar to that outlined in the paragraph on bromates in the chapter on potassium chlorate.

Acidity.—Five grams of the samples shall be dissolved in 100 c. c. of previously boiled distilled water. Delicate neutral litmus paper shall show no acid reaction after 15 minute's immersion.

Insoluble matter.—A weighed sample of about 10 grams shall be dissolved in about 200 c. c. of warm distilled water, and the solution filtered through a previously weighed Gooch crucible. The residue shall then be thoroughly washed, dried at 110° C., and weighed. This weight, divided by the weight of the sample taken, will give the percentage of insoluble matter.

Calcium salts.—One gram of the sample shall be dissolved in distilled water and the calcium and barium salts precipitated by the addition of ammonia, ammonium chloride, ammonium carbonate, and a little ammonium oxalate. After

boiling, the precipitate shall be allowed to stand for two hours, and then filtered off and washed throughly with hot water. The precipitate shall be dissolved on the filter in dilute nitric acid, and the filtrate evaporated to dryness in a 250 c. c. beaker. The residue shall then be gently heated over a free flame until all organic matter has been oxidized. After cooling, a few drops of nitric acid shall be added to convert any oxides that may have formed during the heating into nitrates. The nitric acid shall then be removed by evaporation, the residue dissolved in a small amount of water, and the calcium determined as outlined in the chapter on barium nitrate.

Sodium salts.—Five grams of the sample shall be dissolved in 100 c. c. of distilled water, and ammonium chloride and ammonia shall be added in slight excess, together with solutions of ammonium carbonate and ammonium oxalate in sufficient excess to precipitate all of the barium and calcium present. The precipitation shall be done at the boiling temperature, and the solution allowed to stand for 4 hours before filtering; the precipitate shall be throughly washed with hot water and dissolved in a minimum quantity of dilute hydrochloric acid, and the barium and calcium precipitated as before. The filtrates are combined and evaporated, care being taken to have sufficient hydrochloric acid present to decompose all of the chlorates. Before drying, 5 drops of concentrated sulphuric acid shall be added, and the mass taken to fumes of sulphuric acid, and finally heated until the free sulphuric acid present shall have been driven off. If the residue is discolored, owing to the presence of organic matter, it should be dissolved in a small amount of warm water and filtered. The solution shall then be again evaporated to dryness, using 3 drops of concentrated sulphuric acid, and heated to drive off all the sulphuric acid. The resultant residue of sodium sulphate shall be weighed and reported in terms of sodium oxide as the sodium content.

The following results were obtained from the quantitative tests made upon a sample of commercial barium chlorate:

Moisture: Grams.

Weight taken_____	3
Weight after drying_____	2.9991
Loss in weight_____	.0009

This gives 0.03 per cent.

Barium chlorate: Grams.
  Weight taken_____ 0. 08
  Number of cubic centimeters permanganate used_____ 21. 2
  Number of cubic centimeters of potassium permanga-
    nate equivalent to the 50 c. c. of Mohr's salt used__ 51. 2

Therefore, the available oxygen of the barium chlorate is equal to that contained in 30 c. c. of the $KMnO_4$. The available oxygen contained in 1 c. c. of the potassium permanganate used, 0.0008 grams, when multiplied by the number of cubic centimeters of permanganate consumed, 30, gives 0.024 gram as the weight of available oxygen in the sample. This weight of oxygen multiplied by the factor 3.357 gives the weight of barium chlorate in the part of the sample used, or 0.0805 gram. This weight divided by the weight taken gives 100.71 per cent.

Hypochlorites: Absent.

Bromates: Weight sample taken, 2 grams.

Solution $Na_2S_2O_3$ used equals 0.012685 gram of iodine per cubic centimeter.

Volume of this solution used to titrate the I set free by the bromates equals 0.1 c. c.

Iodine equivalent of $Na_2S_2O_3$ used equals 0.00127 gram; 0.00127 gram I multiplied by factor 0.10495 equals 0.00013 gram Br., and this divided by the weight of the sample equals 0.006 per cent.

Acidity: None.

Insoluble matter: Trace only.

Calcium salts: Grams.
  Weight taken_____ 1
  Weight CaO_____ . 001

This gives 0.1 per cent. CaO.

Sodium salts: Absent.

SPECIFICATIONS.

The results of the research work and the examination of the method of manufacture of barium chlorate make it desirable that the following specifications be adopted for use in military pyrotechnics:

1. The material shall be white or at least show only a slight yellowish tinge.

2. The material shall be odorless.
3. The material shall contain not less than 99.5 per cent. Ba (ClO$_3$)$_2$. H$_2$O.
4. The material shall contain no hypochlorites.
5. The material shall contain not more than 0.01 per cent. bromate compounds figured as bromine.
6. The material shall contain not more than 0.25 per cent. of sodium salts, calculated as the oxide.
7. The material shall contain not more than 0.25 per cent. maximum of calcium salts, calculated as the oxide.
8. When compounded it shall contain not more than 0.2 per cent. of moisture.
9. When compounded the material shall be ground so that all will pass through an 80-mesh sieve and 60 per cent. will pass through a 100-mesh sieve.

DISCUSSION OF SPECIFICATIONS.

The high degree of purity which is attained in the preparation of commercial barium chlorate makes it possible to set the high standard given in the above specifications. Unless the barium chlorate is adulterated, it will not be found to contain the heavy metals or any other impurities to any appreciable extent. With the exception of small amounts of other chlorates, which will not materially interfere with the efficiency of barium chlorate in pyrotechnic compositions, practically no impurities will be found.

The results obtained by the permanganate method for the chlorate determination are invariably over 100 per cent. This is probably due to the presence of small amounts of other chlorates of lower molecular weight. Should the sample be other than pure white in color, it should be regarded with suspicion and carefully investigated to ascertain the reason, as the comercial product usually obtained is pure white.

POTASSIUM PERCHLORATE.

HISTORY.

The history of this substance is intimately connected with that of potassium chlorate and with that of other potassium salts.

The salt was first prepared from potassium chlorate by the action of heat. When the latter compound is heated it first fuses, and then an evolution of oxygen takes place according to the reaction $2KClO_3 = KClO_4 + KCl + 2O$. This is accomplished to the best advantage by heating the potassium chlorate very gradually until the first evolution of oxygen begins. The heating is then continued so as to produce a slow and continuous evolution of the gas until no more is given off without elevating the temperature very materially. Of course, potassium perchlorate itself on being heated to a high temperature breaks down into potassium chloride and oxygen, according to the reaction $KClO_4 = KCl + 4O$. It is, therefore, necessary to stop the reaction before the decomposition of the perchlorate takes place. The potassium perchlorate and potassium chloride are separated very easily by taking advantage of the fact that the chloride is very much more soluble in water than the perchlorate. By using care an extremely pure product may be obtained, but the process is one of laboratory application only, which would be difficult to use on a large scale. Further, there is danger in heating potassium chlorate in large quantities at a time, as it has a tendency to give off its oxygen with explosive violence.

In recent years the salt has been produced in commercial quantities by an electrolytic process. This is simply a continuation of the process used for the production of potassium chlorate. Under suitable conditions the chlorate passes to the perchlorate, which is crystallized out. At the time of

165

writing this book the price of potassium chlorate and potassium perchlorate was the same, and with simple factory adjustment the perchlorate may be obtained in any desired quantity if a sufficient supply of potassium chloride is available.

At the present time potassium perchlorate is not used in the manufacture of military pyrotechnics, but the great advantages of the compound, as compared with chlorates, lead us to believe that its use will become prominent in the future, and for that reason we are including a discussion of the salt in this book.

Potassium perchlorate occurs to a limited extent in nature, being found in small amounts in Chile saltpeter. In 1914, 55 tons were recovered as a by-product in the refining of crude Chile nitrate, and since that time larger amounts have been recovered.

GENERAL PROPERTIES.

The perchlorates are more stable and less sensitive than the chlorates, even though they contain a larger percentage of oxygen. This might be expected when the nature of free chloric and perchloric acids is taken into consideration. Chloric acid is an extremely unstable compound, and this instability is reflected in its salts. Perchloric acid, on the other hand, is comparatively very stable, and may be distilled under diminished pressure without decomposition and with perfect safety. Its salts are also more stable than those of chloric acid. Mixtures containing perchlorates with reducing materials, such as sulphur or sugar, do not begin to be as sensitive to shock as are similar chlorate mixtures, nor does free acid produce the same dangerous decomposition. This may readily be demonstrated by the following experiment:

Prepare a mixture of approximately equal parts of finely powdered potassium chlorate and sugar, grinding the salt separately and mixing the powder with the sugar on a sheet of paper; then prepare a similar mixture of potassium perchlorate and sugar. A drop of concentrated sulphuric acid, when added to the chlorate mixture, will cause immediate decomposition which is violent in its nature, while on the potassium perchlorate mixture it will have no effect. Fric-

tion also will produce an explosion with the chlorate mixture, while the perchlorate mixture will not respond to rubbing or to a moderate blow. There have been many violent explosions produced by grinding together potassium chlorate and any reducing material, and the greatest care must be exercised in handling such compositions. The danger of free acid in connection with chlorate mixtures has been referred to many times. It is probably the most dangerous factor with which the manufacturer of pyrotechnics has to contend, and it can not be too strongly emphasized. It is also evident that any composition containing chlorates which is of such a nature that free acid may be produced during handling or storage will be extremely dangerous. On the other hand, experience has shown that perchlorate mixtures are without these elements of danger, and consequently the study of the substitution of perchlorates for chlorates in pyrotechnic mixtures should be seriously undertaken.

Perchlorates have been used in many explosive mixtures, and it has been found that it is not necessary to have each particle incased in fatty matter, as is the case with chlorate explosives.

The following table and quotations, taken from Marshall on Explosives, show the composition of various explosive mixtures containing perchlorates:

	Permonit I or Gesteins- Per- monite.	Per- monite S. G. P.	Permonite (permitted list).
Potassium perchlorate	30	24.5	31.0–34.0
Nitroglycerin		6.0	3.0– 4.0
Collodion cotton			0.5– 1.0
Ammonium nitrate	40	29.0	39.0–43.0
Sodium nitrate	7		
Trinitrotoluene	15	7.0	11.0–13.0
Sodium chloride		25.0	
Flour	4	4.0	
Starch			5.0– 9.0
Wood meal	3	3.0	1–5– 3.5
Jelly	1	1.0	
Moisture			0.0– 2.5
Influence test ....mm..	70	100	80
Trauzl test ....cc..	320	205	365
Velocity of detonation ......m/sec..	3,470	2,326	
Sensitiveness, 2 kg. weight ......cm..	70	80	20
Sensitiveness, 10 kg. weight ......cm..	5	10	

The "charge limit" of Permonite S. G. P. is 900 g., equivalent to about 570 g. of dynamite No. 1.

"The 'jelly' is a mixture of one part glycerine and 3.5 parts gelatine; the influence test consists in ascertaining the distance over which detonation is conveyed from one 30-cm. cartridge to another lying on the ground. Another German explosive similar to Permonite, but not so powerful, is Wetter-Persalit.

"Another very similar explosive made in Germany is alkalsit. Polarite, a nonfreezing explosive of high power, is used in England as a substitute for gelignite.

"Several explosives containing potassium perchlorate have passed the Rotherham test, and are on the English Permitted List. They differ from the permonites in that they contain a larger proportion of nitroglycerine and wood meal, and the ammonium nitrate has been replaced by oxalate, so that they are not hygroscopic. The result is that instead of an excess of available oxygen they contain a slight deficit.

"The general method of manufacturing these explosives is as follows: The oxalate, perchlorate, and wood meal are all sifted and placed in a pan and mixed together roughly by hand. The nitroglycerine, which has been partially gelatinized with collodion cotton the day before, is poured on top, the last portion of jelly being wiped out with some wood meal which has been kept back for this purpose. The composition is then incorporated in a gelatine incorporator for about an hour at a temperature not higher than 30° C."

	Dynobel.	Neonal.	Neonal No. 1.	Ajax powder.	Swale powder.
Potassium perchlorate...................	27	37	14	37.2	37.5
Nitroglycerine........................	32.5	21	40	22.5	19
Collodion cotton......................	0.7	0.8	2.8	0.8	1
Dinitrotoluene and trinitrotoluene......	....	0.2	....	3.5	4
Ammonium oxalate....................	29.5	25	39	25	28
Wood meal...........................	10.3	16	5	11	10.5
Maximum charge...............ounces.	22	16	30	12	20
Power (swing of bal. pend)......inches.	2.61	2.56	2.51	2.69	2.50

"The addition of nitrotoluenes renders the explosives less liable to freeze.

"A different type of perchlorate explosive is represented by M. B. powder (modified black), which consists of black powder in which part of the saltpeter has been replaced by potassium perchlorate. It is made in much the same way as

safety blasting powder was, that is to say, the ingredients, after a preliminary mixing, are incorporated together in a steam-jacketed pan. On November 25, 1911, a severe fire occurred in the house where this operation was being carried out, whereby three men were killed and one was injured. It was ascribed to friction on dry caked material in the steam-heated incorporator. Another similar explosive is Roslin giant powder.

AMMONIUM-PERCHLORATE EXPLOSIVES.

"As a constituent of an explosive, ammonium perchlorate possesses the advantage that it contains a high proportion of available oxygen and produces only gaseous products, but unfortunately these include the poisonous gas hydrogen chloride. The formation of this can be prevented by adding an equivalent quantity of some substance such as sodium nitrate, which will yield a base to combine with the chlorine. In 1906 the French 'Commission des Substances Explosives' investigated two cheddites containing ammonium perchlorate, and although it was decided not to undertake their manufacture some of the experiments are instructive.[1] The explosives had the compositions:

	I.	II.
"Ammonium perchlorate	82	50
Dinitrotoluene	13	15
Sodium nitrate	--	30
Castor oil	5	5

"No. I burns with dangerous rapidity when ignited, but II is quite safe in this respect. Fabrics impregnated with ammonium perchlorate are more inflammable than when potassium chlorate is used, but not so much so as with sodium chlorate. Ammonium perchlorate is a mild explosive by itself but is only exploded with difficulty and incompletely; at ordinary temperatures it is stable, but at 150° decomposition sets in after a time and proceeds according to the equation: $NH_4ClO_4=Cl+O_2+N+2H_2O$ (gaseous) 38.3 cal. The reaction is apparently autocatalytic.[2] It is very important that ammonium perchlorate be kept quite separate from the

---

[1] P. et S., vol. xiv., pp. 192, 206.

[2] See Girard and Laroche, Moniteur scientifique, April, 1909; S. S., 1910, p. 134.

chlorates of sodium and potassium, as dangerous double decompositions are liable to occur. Ammonium perchlorate has about the same degree of sensitiveness to impact as picric acid; a 5 kg. weight falling 20 c. c. causes explosion sometimes. As in the case of other cheddites, the velocity of detonation rises with increase of density to a maximum, after which it falls in consequence of the diminution of the sensitiveness to detonation.

"A number of explosives of this type were made in Belgium under the name of Yonckites. One of these, No. 10bis, is on the Belgian list of Explosives S. G. P. No. 13 is of a more brisant type:

	10bis.	13.
Ammonium perchlorate	25	20
Ammonium nitrate	30	27
Sodium nitrate	15	27
Barium nitrate	--	6
Trinitrotoluene	10	20
Sodium chloride	20	--

" The ' charge limite ' of 10bis is 900 g., equivalent to 540 g. dynamite No. 1. To make these explosives, the perchlorate and nitrates of sodium and barium are milled together, as also are the ammonium nitrate and trinitrotoluene. The two mixtures are then incorporated together in a Pfleiderer machine. These explosives were examined by the French Commission des Substances Explosives, but it was decided that they possessed no marked advantage over the cheddites.[1]

"An explosive which is not being used extensively is Blastine, in which ammonium perchlorate and sodium nitrate are mixed with the combustible matters, dinitrotoluene and paraffin wax."

The above is largely quoted from Marshall on Explosives.

PHYSICAL PROPERTIES.

Color and odor.—The salt is colorless and odorless.

Solubility.—One part is soluble in 22 parts of water at ordinary temperatures and in 4 parts of water at 100° C.

Hygroscopicity.—The substance is not hygroscopic and does not alter on exposure to the air.

---

[1] P. et S., vol. xvii, p. 170; Vennin et Chesneau, p. 362.

Flame color.—It imparts the characteristic violet color of potassium salts to the flame.

Fusibility.—It fuses at 610° C.

Hardness.—It is a crystalline salt which is soft and easily ground.

Specific gravity.—The specific gravity is 2.52

CHEMICAL PROPERTIES.

GENERAL NATURE.

Potassium perchlorate has the molecular weight 138.56. This is made up of one atom of potassium with the atomic weight of 39.1, one atom of chlorine with an atomic weight of 35.46, and 4 atoms of oxygen with the combined atomic weight of 64. It is the potassium salt of perchloric acid and has the formula $KClO_4$. It carries no water of crystallization. When heated, it gives off oxygen readily, to which fact it owes its effectiveness. It contains 46.19 per cent. available oxygen. The oxygen content of potassium chlorate is but 39.17 per cent., from which it is evident that potassium perchlorate contains approximately 1⅓ as much oxygen, molecule for molecule, as potassium chlorate.

FUNCTION IN PYROTECHNIC PIECES.

If compositions containing potassium perchlorate should be adopted for pyrotechnic use, it would play the same part as potassium chlorate does in the mixtures which have been hertofore described, that is to say, it would furnish the oxygen necessary. As potassium perchlorate is a salt of a strong acid, it would not be affected by the weak organic acids which form the principal part of many of the cheaper gums, such as rosin, and if experiment shows that potassium perchlorate in connection with this gum, or some similar substance, forms compositions which are stable in their nature, the use of shellac may be avoided. This, of course, would be a great advantage from the standpoint of economy, as well as availability of supply during a time of war. The use of potassium perchlorate, therefore, is undoubtedly one of the most important subjects to be investigated in the further development of military pyrotechnics.

METHODS OF ANALYSIS.

The following methods for the analysis of potassium perchlorate are based on the assumption that it is the reasonably pure commercial article which is now available.

QUALITATIVE TESTS.

Flame test.—This test should be made in the ordinary manner by means of a platinum wire moistened with concentrated hydrochloric acid, dipped in the powdered salt and heated with a Bunsen burner. This test is made for the purpose of determining the purity of the salt in a very general way, in order to indicate the method of procedure.

Acidity.—Delicate neutral litmus paper, when inserted in a solution of the salt, shall show no acid reaction after an immersion of 15 minutes.

Sulphates.—A solution of the salt shall be acidified with dilute hydrochloric acid, heated, and a solution of barium chloride added. The formation of a white precipitate of barium sulphate will indicate the presence of sulphates.

Salts of calcium.—To a hot solution of the salt ammonium chloride, ammonia, and ammonium oxalate shall be added. The formation of a white precipitate will indicate the presence of soluble salts of calcium.

Salts of magnesium.—If a white precipitate, indicating the presence of salts of calcium, is formed, it shall be filtered off. To the filtrate a small amount of ammonium-phosphate solution shall be added, together with a volume of concentrated ammonia equal to one-third the total volume of the solution. The solution shall be allowed to stand in a cool place for at least 12 hours. The presence of salts of magnesium will be indicated by the formation of a white crystalline precipitate of ammonium-magnesium phosphate.

Chlorides.—A few drops of a solution of silver nitrate shall be added to a solution of the potassium perchlorate. The formation of a white precipitate of silver chloride will indicate the presence of chlorides in the original material.

The following results were obtained from the qualitative tests made on a sample of commercial potassium perchlorate:

Flame test: No sodium or calcium in appreciable amounts indicated.

Acidity: Neutral.
Sulphates: Absent.
Salts of calcium: Absent.
Salts of magnesium: Absent.
Chlorides: Traces only.

QUANTITATIVE TESTS.

Moisture.—A weighed sample of from 3 to 5 grams shall be spread out on a 3-inch watch glass and dried to constant weight in an air bath at 130° C. The loss in weight divided by the weight taken will give the percentage of moisture.

Insoluble matter.—From 3 to 5 grams of the salt shall be dissolved in hot water and filtered through a previously weighed Gooch crucible. The residue shall then be thoroughly washed with hot water, dried, and weighed. The weight of the residue divided by the weight taken will give the percentage of insoluble matter in the sample.

Chlorides.—If the presence of chlorides has been indicated by the qualitative test, 5 drops of a 5 per cent. solution of potassium chromate shall be added to the filtrate from the insoluble matter above. The chlorides present shall then be titrated with a one-fiftieth-normal solution of pure silver nitrate, prepared by dissolving 3.3978 grams of silver nitrate in 1 liter of water. Each cubic centimeter of this solution will be equivalent to 0.000709 gram of chlorine, consequently the volume of solution required for the titration multiplied by 0.000709 will give the weight of chlorine contained in the sample as chlorides. This weight divided by the weight of the sample will give the percentage of chlorine contained as chlorides.

Sulphates.—Dissolve 5 grams of the potassium perchlorate in hot water, filtering off any insoluble matter; to the filtrate, which should have a volume of 400 c. c., 2 c. c. of concentrated hydrochloric acid shall be added, followed by 10 c. c. of a hot 10 per cent. solution of barium chloride; the solution shall be boiled for a few minutes, allowed to stand for two hours, the precipitate of barium sulphate filtered off through ashless filter paper, and the precipitate washed with hot water until the washings give no test for chlorides with silver-nitrate solution. The precipitate shall then be ignited

and weighed. As has been previously stated, the weight of barium sulphate multiplied by the factor 0.1373 will give the weight of sulphur in the sample in the form of sulphates, and this weight, divided by the weight of the sample taken, will give the percentage of the sulphur content. Sulphates are not ordinarily present in commercial potassium perchlorate, but the above method is applicable in case they should be found.

Calcium salts.—If calcium is indicated in the qualitative test, a solution of 5 grams of the salt shall be boiled with a few drops of hydrochloric acid and the solution filtered if necessary. A solution of ammonium chloride, ammonia, and ammonium oxalate shall then be added to the hot solution, which shall be boiled for a few minutes and allowed to stand for at least two hours. The precipitate of calcium oxalate shall then be treated as outlined in the chapter on strontium carbonate.

Magnesium salts.—To the filtrate from the calcium oxalate a small amount of ammonium phosphate shall be added, together with concentrated ammonia equal to one-third the total volume of solution. The solution shall be allowed to stand in a cool place for at least 12 hours, the magnesium, ammonium phosphate filtered off, washed with a cold solution of ammonium chloride, ignited and weighed as magnesium pyrophosphate, $Mg_2P_2O_7$. As magnesium pyrophosphate, having the molecular weight 222.72, is equivalent to 2 molecules of magnesium oxide, MgO having a total molecular weight of 80.64, it is evident that the weight of magnesium pyrophosphate obtained, multiplied by the fraction $\frac{80.64}{222.72}$ or 0.36207, will give the magnesium-oxide content of the sample, and this weight, divided by the weight of the sample taken, will give the percentage of magnesium oxide obtained.

Sodium salts.—Ignite 1 gram of the potassium perchlorate in a silica crucible until the evolution of oxygen has ceased, finally bringing the mass to a state of quiet fusion. The potassium chloride thus obtained shall be converted into the nitrate by repeated evaporations with nitric acid to constant weight. When this conversion is complete, the sodium shall be determined by the use of Ball's reagent, as indicated in the chapter on potassium nitrate.

Bromates, chlorates, and hypochlorites.—These substances shall be determined as indicated in the chapter on potassium chlorate.

Potassium perchlorate.—One gram of the potassium perchlorate shall be carefully fused with 5 grams of sodium carbonate, in a platinum crucible, thus converting it completely into potasium chloride. The melt shall then be extracted with hot water and filtered if necessary. The filtrate shall be rendered slightly acid with pure nitric acid and then the chlorine preciptated as silver chloride by the use of an excess of silver-nitrate solution. The solution shall be warmed until the supernatent liquor is clear, and then filtered through a previously weighed Gooch crucible. The silver chloride shall then be thoroughly washed with hot water, dried at 120° C., and weighed.

One molecule of silver chloride is equivalent to 1 molecule of potassium chloride, which in turn is equivalent to 1 molecule of potassium perchlorate. Silver chloride has the molecular weight 143.34 and potassium perchlorate the molecular weight 138.56, consequently the weight of the silver chloride obtained, multiplied by the fraction $\frac{138.56}{143.34}$ or 0.9667, will give the weight of potassium perchlorate in the sample, and this weight, divided by the weight taken, will give the percentage of potassium perchlorate.

The above method will be applicable only for the analysis of samples containing no chlorides, hypochlorites, chlorates, or bromates, as the first three of these substances will form silver chloride, while the bromate will yield silver bromide. In case any of these substances are present, the following procedure shall be followed:

One gram of the material shall be boiled with concentrated hydrochloric acid in excess, finally evaporating to dryness. This operation will decompose the hypochlorites, chlorates, and bromates, but will not affect the perchlorates. The residue shall now be dissolved in hot water, and the chlorides present precipitated by the addition of a slight excess of a silver-nitrate solution; finally, the excess of silver nitrate shall be precipitated by the addition of a very slight excess of hydrochloric acid. The solution shall now be allowed to stand until the precipitate of silver chloride has settled. It shall then be filtered and the residue washed. The com-

bined filtrate and wash water shall be evaporated to a very small volume in a silica or porcelain evaporating dish and finally transferred to a platinum crucible, in which the evaporation shall be completed. After evaporation the residue shall be gently heated to drive off the last traces of acid. Five grams of pure sodium carbonate shall now be added and the crucible heated to dull redness, until the fused mass is quiescent. During this fusion the potassium perchlorate will give off its oxygen, forming potassium chloride, the sodium carbonate being used to prevent loss by boiling and spattering. The melt shall then be extracted in hot water and the chlorine determined as indicated in the last procedure.

DISCUSSION OF ANALYTICAL METHODS.

It will be generally found that commercial potassium perchlorate will not contain sulphates, compounds of calcium and magnesium, chlorides, hypochlorites, chlorates, or bromates in anything more than mere traces, consequently the simple procedure for the determination of potassium perchlorate by direct fusion of the sample with sodium carbonate will generally prove to be all that is required. Further, salts of sodium are not usually found in potassium perchlorate; the material is also free from insoluble matter; therefore, the usual determinations to be made include only those of moisture and potassium perchlorate.

ANALYTICAL RESULTS.

Moisture:

	Grams.
Weight taken	3
Weight after drying	2.9991
Loss in weight	.0009

This weight, divided by the weight taken, equals 0.03 per cent.

Insoluble matter: Absent.
Chlorides: Bare trace only.
Sulphates: Absent.
Calcium salts: Absent.
Magnesium salts: Absent.
Sodium salts: Trace only.

Bromates: Trace.
Chlorates: Trace.
Hypochlorites: Absent.
Potassium perchlorate:

	Gram.
Weight of sample taken	0. 5
Weight of silver chloride obtained	. 516

This multiplied by the factor 0.9667 gives 0.4988 gram as the weight of potassium perchlorate in the sample. This divided by the weight of the sample taken gives 99.76 per cent.

SPECIFICATIONS.

In connection with the investigations made upon potassium perchlorate, we beg to recommend that the following specifications be adopted for the potassium perchlorate to be used in military pyrotechnics:

1. The material shall be white in color.
2. The material shall be odorless.
3. When compounded, the material shall be ground so that all will pass through an 80-mesh sieve and 60 per cent. will pass through a 100-mesh sieve.
4. The material shall contain not less than 99 per cent. of potassium perchlorate.
5. The material shall contain not more than 0.2 per cent. moisture when compounded.
6. The dry material shall not contain more than 0.2 per cent. of calcium or magnesium salts, or of both together, calculated as oxides.
7. The material shall not contain more than 0.1 per cent. of sodium salts, calculated as Na_2O.
8. The material shall contain not more than 0.1 per cent. of bromates figured as bromine.

DISCUSSION OF SPECIFICATIONS.

The analysis of the commercial sample of potassium perchlorate clearly indicates that it is the remarkably pure article which might be expected from its method of manufacture. We believe that the specifications given are well within the limits of reason, and that it would not be difficult to obtain the salt in large quantities of the grade described.

CHAPTER XII.

SHELLAC.

HISTORY AND METHODS OF MANUFACTURE.

The word is derived from " shell," referring to the shell-like form in which it occurs, and " lac," an Indian term meaning one hundred thousand, which relates to the swarms of insects through whose life process it is produced. It is popularly supposed to be the dried exudation of a tree which has been wounded by the sting of the lac insect. Following the injury, the gum is supposed to gather on the surface of the bark and dry out in a manner similar to that which causes the formation of pitch, where the bark of the pitch-pine tree has been wounded.

This theory of the formation of the material is not correct, as it is the secretion of the lac insect produced during its process of metabolism, just as honey and beeswax result from the modification of the nectar of flowers by the bee. The name has reference to the shell form of the secretion as used in commerce, for shellac is a manufactured article. Lac, however, is the original product as gathered from the trees. It is stated that lac occurs only in northeastern India and in adjacent countries; the shipments originate from Calcutta. The insect producing the gum is called Tacchardia Lacca, and belongs to the scale family. It is without wings, has 6 legs and is only $\frac{1}{40}$ of an inch in length. It is of a red or orange color and too weak to travel far. Whenever the number of the insects becomes greater than a twig can support, the method they employ in seeking a new habitation is by dropping; only those fortunate enough to alight on a fresh twig below are able to continue their life; the others perish.

The insect, after attaching itself to a twig, begins at once to absorb the sap, provided the bark is tender enough for it to pierce, and the exudation of the lac begins. The insects are in the habit of locating close to each other, so that the in-

178

dividual particles of lac soon begin to coalesce; this results in a ring of gum around the twig, which is several times the diameter of the twig itself. It is possible that the insect owes its continued existence to the formation of this gum which acts as a protective covering and shields it from the many agencies which would otherwise destroy it. As it is, many animals, including monkeys and insects, feed upon the Tacchardia Lacca or upon the sweet incrustation. Swarming takes places twice a year, in the months of July and December, two and one-half months being required for the maturing of the insect. The male insect leaves his cell while the female stays in place. The female is provided with three groups of fibers, which, when covered by the incrustation, form tubes that are used as air conduits, to permit fertilization by the male, who then dies, and to furnish an outlet for the new brood hatched from the eggs laid by the mother. The life of the female is about three and one-half months longer than that of the male. She lays about 1,000 eggs, and by the time the new brood has hatched, the female dies and her body dries up, leaving only the skin. This new brood escapes as has been indicated, and a new cycle begins.

The number of trees producing the gum is often increased by moving twigs infected with the insect to other trees. The natives gather the incrusted twigs twice a year, and the stick-lac of commerce is produced by breaking them up into short sections. The lac insect thrives principally on the varieties of trees known as Kusum and Palas, but it is known to exist on about 88 different kinds of trees, the value of the product depending not only upon the kind of trees on which the insect is growing, but on climatic conditions as well. No attempt is made, however, to classify the "stick-lac" according to the variety of the tree from which it is produced.

Seed-lac consists of ruby-red or orange-colored grains about the size of wheat. It is made from stick-lac by removing the wood and a part of the coloring material by crushing and washing. During this washing process it is found that a substance known as lac-lye separates, and at one time this was of value in the dye industry as a substitute for cochineal.

The shellac of commerce is made from dried seed-lac which is placed, with a certain proportion of orpiment, in bags and heated over a charcoal fire until the gum melts and runs through the cloth. While in a molten condition, the bag is constricted by twisting, thus forcing the gum through the fibers of the cloth; the gum is then removed by scraping. It is next heated until it becomes plastic, stretched out over a cylinder which is heated with hot water, and finally pulled out into a thin sheet, which is either a light or dark orange in color. These sheets, when broken into flakes, constitute the shellac of commerce. The color and transparency, flatness and strength of the flakes, and freedom from adulteration, afford the factors for commercial grading. The amount of orpiment used varies from 0.05 to 0.25 per cent., its function being to impart the desired light-yellow color. Many grades of shellac are handled commercially. Those found on the daily market are known as:

D. C.
V. S. O.
Diamond I.
Superfine orange.
Fine orange.
Medium orange.
T. N.
A. C. garnet.
Button.
Bleached ground.
Bleached bone dry.

Those free from rosin are marked:

D. C. (David Campbell).
V. S. O. (Very superior orange).
Diamond I.
Superfine.
Fine.
Good.

The lower grade, which constitutes the majority of the product, is known as T. N. It may contain 5 per cent. or more of rosin, unless marked pure by the U. S. standard. T. N. marked U. S. S. A. does not contain over 3 per cent. rosin.

A. C. garnet is manufactured from the refuse lac remaining in the bags after the squeezing-out process. This contains from 30 to 50 per cent. sand and insoluble matter. It is extracted with alcohol. After evaporating the alcohol the fused lac is run out on a table or metal slab and constitutes the A. C. garnet grade mentioned in the table. In a pure form it is free from rosin, but it ordinarily contains from 8 to 10 per cent. rosin. The color is dark-purple red; other grades containing 18 per cent. and more rosin, which are almost black in color, may be obtained from the refuse lac by treatment with dilute soda, followed by subsequent precipitation by acid. These grades, however, are not on the market at the present time. The better grades are shipped in wooden cases lined with cloth and covered on the outside with burlap, the usual net weight being 2 maunds or 164 pounds net.

The T. N. grade is usually packed in double burlap bags of the same weight.

The shipments from Calcutta pass through the Red Sea and Suez Canal, and the heat of the climate, coupled with the lack of ventilation in the holds of the ships, often causes a partial solidification of the flakes of the gum, consequently on arrival at its port of final destination, it is referred to as "free," "caught," "matted," "finely matted," or "blocked." Two crops are gathered. The spring crop, known as "Bisakke," which is the larger, contains the greater part of the T. N. grade. The "Koosmie," or fall crop, furnishes the larger portion of the better grades, and as the weather during shipment is cooler, the material arrives in a better condition. The T. N. grade is the only one used for pyrotechnic purposes. The many other commercial grades will not be considered.

AVAILABILITY OF SUPPLY.

The yearly output of all grades is about 41,000,000 pounds, of which more than one-half comes to the United States. No figures are available as to the relative amounts of the different grades, but the majority of the product shipped is of the T. N. grade. Shellac is the only product used in pyrotechnics which is exclusively foreign in its origin, and there has yet

appeared no substitute for it which can be derived from native sources. Any interference with shipping facilities would utterly cut off our supply and a substitute should be sought for and developed if possible.

USES OTHER THAN IN PYROTECHNICS.

Shellac has many uses in every-day life. The principal use, of course, is in the manufacture of varnishes. It is also used as a binder in various composition goods, such as buttons, telephone receivers, phonograph records, electric insulators, and in the preparation of sealing wax; cut in alkalies, it is used as a dressing on leather and patent leather.

PHYSICAL PROPERTIES.

Color and odor.—The technical term applied by the pyrotechnical manufacturers to the grade of shellac used by them, T. N., describes the color of the commercial article. The material is without odor.

Solubility.—Like most other gums, shellac is comparatively insoluble in water. It is however readily soluble in alcohol and in many of the other solvents commonly used for dissolving organic substances.

Hygroscopicity.—The substance is not hygroscopic nor does it suffer alteration on exposure to the air.

Flame color.—It imparts no color to the flame.

Fusibility.—Owing to the fact that shellac is not a pure substance, but consists of a varied mixture of several components, it has no definite melting point. As described in the method of manufacture, however, it softens so that it may be drawn out into thin sheets at a relatively low temperature.

Hardness.—It is a soft brittle gum, which may be easily ground.

Specific gravity.—It has a specific gravity of from 1.113 to 1.214.

GENERAL PROPERTIES.

The principal constituents of the gum are as follows:

Shellac contains up to 6 per cent. of wax, from 2 to 6 per cent. of laccin pigment, small quantities of laccainic acid (which is a constituent of the lac dye), traces of the higher

fatty acids, a yellow coloring matter called Erythrolaccin, which is apparently a hydroxymethylanthroquinone, and a small quantity of an odorous substance of the nature of the resenes. Sixty-five per cent., however, is the aleuritic ester of an unstable resinotannol.

GENERAL NATURE.

The pyrotechnic manufacturers claim that the principal advantage in the use of shellac over other cheaper gums, such as gum kauri and rosin, in connection with all chlorates, is due to the fact that the shellac either contains less free acid than other gums, or that the acid which it does contain is not of such a nature as to be dangerous when compounded with chlorates. Much has been said in the preceding chapters concerning the danger of chlorate mixtures which contain free acid at the time of compounding, or in which the conditions might be such as to generate free acid after the pieces containing the compositions were manufactured. It has been the universal practice to use shellac in chlorate mixtures, even though it is far more expensive than other gums, actual experience having shown the great stability of shellac-chlorate compositions as compared with compositions containing chlorates and other gums. It should also be noted that the physical nature of ground shellac is such that, when it is used in compositions which are subjected to compression, the briquettes produced are hard, firm masses which retain their shape during handling. This is a very necessary and desirable quality. In some cases, a greater firmness is obtained by moistening the material with a little alcohol before subjecting it to compression. The finished articles become very hard after the alcohol is removed by drying. It might be possible, also, to decrease the porosity of the compressed materials by the use of sufficient alcohol, so that the interstices between the particles should be filled with the thick alcoholic colloid. This should cause the compositions to burn longer than if the pores were not so filled.

FUNCTION IN PYROTECHNIC PIECES.

As has been indicated, shellac plays a very important part, particularly in the physical character of the compressed com-

positions containing it, in which it is a binder. Chemically it serves as the fuel to be consumed by the oxidizers present, thus affording the necessary heat. At the present time it is used in the rocket red signal composition, containing—

	Per cent.
Strontium nitrate	66.6
Potassium chlorate	25
Orange shellac	8.4

In the rocket green signal composition, containing—

	Per cent.
Barium chlorate	55.5
Barium nitrate	33.3
Orange shellac	11.2

In the red rifle-light and red Véry-light composition, containing—

	Per cent.
Potassium chlorate	72.7
Strontium carbonate	15.2
Orange shellac	12.1

In the green rifle-light and green Véry-light composition, containing—

	Per cent.
Barium chlorate	90
Orange shellac	10

In the red position-light composition, containing—

	Per cent.
Potassium chlorate	37.5
Strontium nitrate	50
Orange shellac	12.5

In the green position-light composition, containing—

	Per cent.
Barium chlorate	23.2
Barium nitrate	59
Potassium chlorate	6.3
Orange shellac	10.5
Stearin	1

In the aëroplane-flare first fire, containing—

	Per cent.
Barium nitrate	44.5
Saltpeter	33.3
Orange shellac	11.1
Sulphur	11.1

It is also used in the form of a solution in order to render the wing-tip-flare red-tinge composition adhesive. This composition contains—

	Per cent.
Strontium nitrate	66. 6
Sulphur	16. 7
Aluminum	16. 7

In connection with meal powder it enters the prime composition containing—

	Per cent.
Meal powder	97
Orange shellac	3

From the above it will be seen that shellac is one of the most important constituents used in the present practice for the manufacture of military pyrotechnics. Any interference with our supply of this material might have a very serious result, and substitutes for it should be devised if possible. If a substitute can be found it should be available in the requisite quantities within the United States and should be as cheap in price as possible. We regard the development of some such substitute as one of the most important problems for investigation in the field of military pyrotechnics, and believe that this work should be taken up simultaneously with the investigations on the substitution of perchlorates for chlorates.

QUALITATIVE TEST.

The only qualitative test which will be of value in connection with the powdered shellac to be used for pyrotechnic work, is the investigation of the sand and grit which it may contain. About 5 grams should be stirred with cold water; the particles of the gum will float, while sand and grit will sink.

QUANTITATIVE TESTS.

The quantitative determinations are based on the assumption that the shellac investigated is the commercial product known as the T. N. grade.

Moisture.—A weighed sample of about 3 grams shall be spread out on a 3-inch watch glass and dried to constant

weight is a desiccator over sulphuric acid. The loss in weight thus determined, divided by the weight taken, will give the percentage of moisture in the sample.

Insoluble matter.—Five grams shall be dissolved in 100 c. c. of ethyl alcohol (95 per cent.) by digesting in a water bath for 2 hours, or until solution is complete. The solution shall then be filtered through a Gooch crucible, the residue washed with hot alcohol, dried at 100° C. and weighed. This weight, divided by the weight of the sample taken, will give the percentage of insoluble matter.

Ash.—The insoluble residue in the Gooch crucible shall be ignited until all organic matter has been completely burned off. It shall then be weighed. The weight thus obtained, divided by the weight of the sample taken, will give the percentage of ash.·

Resin.—The amount of resin in shellac shall be determined by the " Iodine number." The determination of the " Iodine number " shall be according to the method adopted by the subcommittee on shellac analysis, published in the Journal of the American Chemical Society, volume 29, page 1221, 1907.

The " iodine number" or percentage of iodine absorbed.—The following is an abstract of the report of the subcommittee on shellac analysis of the American Chemical Society, published in the second part of volume 29 of the Journal of the American Chemical Society, on page 1221, 1907:

This method depends upon the different powers of shellac and rosin to unite with the halogens. These differences being expressed in the " Iodine number " or percentage of iodine absorbed. The committee found that the other properties of the two substances, shellac and rosin, such as solubility, acidity or the Koettstorfer's number, did not yield results sufficiently reliable for general use. It was found that the absorption of halogens by both shellac and rosin is a phenomenon of substitution and not addition, as is the case with fats. The amount of hydrogen replaced by halogen in rosin depends upon the length of time that the reagent acts, and also upon the excess of the reagent, the temperature, and the relation of the volume of solution to the amount of substance treated.

After a long series of experiments, the committee arrived at the following standard procedure, which is a modification of the Wijs process, and has the advantage of requiring but two hours for completion.

Solutions required.—Iodine monochloride containing 13 grams of iodine per liter, in glacial acetic acid, having a melting point of from 14.7° to 15° C., which is free from reducing materials.

This is known as Wijs solution: A solution of sodium thiosulphate shall be made by dissolving 24.83 grams of the pure salt in 1000 c. c. water. Pure chloroform and a starch solution are also necessary.

The preparation of the ICl solution presents no difficulty, but must be done with care, as it must contain no appreciable amount of either iodine or chlorine in excess, although it may contain a very small amount of free iodine. No free chlorine whatever is permissible. It shall be prepared by dissolving the iodine in the whole of the acetic acid, heating gently to assist solution if necessary. Set aside a small portion of the solution, and pass pure dry chlorine gas, which has been freed from HCl by washing, through the solution until the iodine color just disappears. The solution will now contain a slight excess of chlorine, and the small proportion of the original solution of iodine which was set aside shall be used to combine with this excess.

Introduce 0.2 gram ground shellac into a 250 c. c. dry clear-glass bottle having a ground-glass stopper, add 20 c. c. acetic acid and warm gently until the shellac passes into solution, with the exception of wax. Pure shellac is rather difficultly soluble and the more rosin there is present the less time will be required for the solution. Add 10 c. c. chloroform, cool to from 21° to 24° C.; add 20 c. c. of Wijs solution from a pipette having a rather small delivery aperture. The bottle shall be closed, put in a dark place, and the time noted. In one hour add 10 c. c. 10 per cent. KI solution and titrate at once with the thiosulphate solution, of which 25 c. c. to 30 c. c. may be run in immediately unless the shellac is very impure, in which case a portion should be added immediately and the remainder gradually, accompanied by vigorous shaking; just before the end a little starch solution shall be added. The end point is sharp as the reaction prod-

ucts of shellac remain in solution in the chloroform; some-times a color will return after 30 seconds, which need not be considered. Having previously determined the equivalent of the thiosulphate solution to the iodine solution, the vol-ume of the iodine solution consumed, and consequently the weight of iodine consumed by the sample, is obtained. This weight divided by the weight of the sample taken will give the per cent. of iodine absorbed or the "Iodine number."

A blank determination, using 20 c. c. Wijs solution, 20 c. c. acetic acid, 10 c. c. of chloroform, and 10 c. c. 10 per cent. KI solution shall be run. This is necessary on account of the well-known effect of temperature changes on the vol-ume and possible loss of strength of the Wijs solution. With grossly adulterated shellac 0.15 gram or even 0.1 gram of the sample shall be used in order that the excess of ICl may not be too greatly reduced. In any event, if less than 25 c. c. of the thiosulphate solution is required for excess, another determination should be run with a smaller amount of the sample.

During dry weather the handling incident to the weigh-ing out of the sample may produce electrification, conse-quently the material should be allowed to stand on the bal-ance pan for some time before completing the weighing.

Owing to the fact that the glacial acetic acid used may solidify from time to time at the temperature of the room, it is necessary that both the Wijs solution and the acetic acid should be thoroughly shaken before use.

It is important that the acetic acid should be of the right strength. The determination of its melting point affords the easiest method for determinining this strength. In order to do this, an 8-inch test tube shall be filled half full with the acid to be tested and chilled rapidly to 10° or 11° C., and a delicate and accurate thermometer, graduated to tenths of one degree, shall be suspended in the chilled acid. The test tube containing the acid shall be placed in a wider test tube, closed by a cork, through which the smaller test tube is in-serted. The whole arrangement shall be chilled by being im-mersed in ice water. The acetic acid begins to crystallize in a few minutes, and the temperature of the supercooled acid rises to its melting point, where it remains stationary for some time. The acid in the test tube should not begin to

crystallize until some minutes after it has been chilled in cold water and placed in the larger tube; after it begins to crystallize, before the cooled acid has had time to become of uniform temperature throughout, it shall be stirred well with the thermometer before the crystallizing process has gone too far. The melting point of acetic acid containing various percentages of water has been determined by Rudorff. (See Beilstein, 3d edition, vol. 1, pp. 339, 400.)

100 per cent	16.75 C.
99 per cent	15.65 C.
99 per cent	14.80 C.
97.1 per cent	11.95 C.
95.2 per cent	9.40 C.

This committee did much work before it was determined that the strength of the acetic acid was essential to uniform results, and the importance of this factor in the determination is insisted upon. Further, the conditions of weight, volume, time and temperature are the result of a long series of experiments, and their importance also is emphasized.

Unbleached shellac shows an iodine absorption varying from 15 to 18 by this method, and no pure shellacs show a higher absorption than 18, which is set as the standard figure for pure shellac by the committee. Rosin alone shows figures that vary from about 175 in the darkest varieties to about 260 in the very lightest color, or W. W. grade, based on the above method of absorption determination. Of course, any grade of rosin might be mixed with shellac, but those actually used seem to be the intermediate ones whose iodine figures by this method range between 200 and 225. The committee accepted it as a principle that such a standard method as this should work so that its inaccuracies would tend toward favoring the seller, rather than of toward condemning too severely the article sold. Consequently the standard of 228 was adopted for rosin, although in the case of the dark-colored shellacs, the rosin used for an adulterant may be dark, and therefore have a somewhat lower iodine figure. Using the figures 18 for shellac and 228 for rosin, this method may give a slightly lower percentage of rosin than is actually present.

If   Y=per cent. rosin in the sample.
       M=iodine per cent. or number of shellac.
       N=iodine per cent. or number of rosin.
       A=iodine per cent. or number of mixture.

Then $Y = 100 \dfrac{(A-M)}{(N-M)}$

ANALYTICAL RESULTS.

[*Example.*]

Moisture:

Grams.

Weight taken _____ 3
Loss in weight _____ .0384

This divided by the weight taken equals 1.28 per cent.

Insoluble matter:

Grams.

Weight taken _____ 5
Weight of insoluble matter _____ 1.882

This divided by the weight taken equals 3.66 per cent.

Ash:

Grams.

Weight taken _____ 5
Weight of ash _____ .0702

This weight divided by the weight taken equals 1.4 per cent.

Iodine number: 1 c. c. of one-tenth-normal $Na_2S_2O_3$ used equals 0.006342 grams iodine in the form of iodine mono-chloride.

Grams.

Weight of sample taken _____ 0.2

Number of cubic centimeters of thiosulphate solution taken by the blank was 42.4. Number of cubic centimeters of thiosulphate solution taken with the sample, 34.6. Therefore the iodine consumed equals 7.8 c. c. of sodium-thiosulphate solution. 0.006342 multiplied by 7.8 gives 0.04947 as the amount of iodine consumed. This divided by the weight taken gives 24.7 as the iodine-absorption number.

SPECIFICATIONS.

From the considerations set forth in the analytical work, the following specifications should be made with regard to the shellac to be used for pyrotechnic purposes. This is based on the assumption that the shellac under consideration is the ordinary T. N. now being used in military pyrotechnics.

1. The sample shall not contain more than 1.5 per cent. of moisture when compounded.
2. The sample shall not contain more than 4 per cent. of matter insoluble in ethyl alcohol.
3. The sample shall not contain more than 1.5 per cent. of ash.
4. The iodine number of the sample shall not be more than 25.
5. The sample shall not contain any appreciable amount of sand or grit that will settle in water.

DISCUSSION OF SPECIFICATIONS.

With regard to these specifications, we say that we have allowed for a greater iodine absorption number than the committee, who set a standard of 18 for pure shellac.

We have allowed greater latitude in this respect on account of the fact that the shellac used is one of the lower grades and the conditions of its use do not require the freedom from rosin that is necessary for the shellac that is to be used for such purposes as the manufacture of varnish, etc. Small amounts of rosin occur naturally in this grade of shellac, and the standard set for the iodine number, 25, is based upon the results of a number of analyses. Further, the limits set on the moisture, insoluble matter, and ash are based upon the results obtained from the analysis of several samples. They are planned to render possible the use of almost any commercial shellac that has not been grossly adulterated or that has not been prepared with great carelessness.

CHAPTER XIII.

DEXTRIN.

METHOD OF MANUFACTURE.

Commercial dextrin or "British gum" is now manufactured extensively by moistening starch or flour with a mixture of dilute nitric and hydrochloric acid and then exposing it to a temperature of from 100° to 125° C. Either nitric or hydrochloric acid may be substituted for the mixture, or oxalic acid may be employed. Dextrin is a white, yellowish, or light-brown powder. It consists largely of erythro-dextrin, and hence its aqueous solution gives a brown coloration with iodine, unless this reaction is obscured by the blue color produced by a considerable proportion of soluble starch. It is not unusual to find a considerable quantity of soluble starch in commercial dextrin. For most purposes, dextrin which contains more than 15 per cent. of starch is undesirable. This does not necessarily make the dextrin unavailable for pyrotechnic use, but is a guide in forming a judgment as to the amount of starch which may be present; a considerably larger amount of soluble starch would impair the gumming properties of the dextrin and would make its use in pyrotechnic work unsuitable.

Dextrin may be prepared by heating starch or flour at temperatures varying from 210° to 280° C. until it acquires a yellow or brown color. This conversion is greatly facilitated by the addition of dilute nitric acid and then slowly drying the paste and heating it for some time between 110° and 150° C.

Another method of preparation is by boiling starch with dilute sulphuric acid until the cooled liquid no longer gives any coloration with a solution of iodine. Still another method of preparation is by treating gelatinized starch with warm water and a small quantity of malt extract.

CHEMICAL NATURE.

Dextrin has the formula $(C_6H_{10}O_5)_x$ or $(C_6H_{10}O_5)_x$ H_2O. Chemically this compound is known as amylin.

Several varieties of amylin or dextrin exist, being apparently formed by the breaking up of the highly complex starch molecule by treatment with dilute acids or ferments. There are no ready methods to distinguish the different varieties of dextrin with certainty, except that one kind, or possibly class, of dextrin gives a reddish-brown color with a solution of iodine, while the other produces no coloration. The erythro-dextrin, the kind that gives the reddish-brown color with iodine, is tested as follows:

A very weak solution of iodine in potassium iodide is divided into two parts and placed in adjacent test tubes, the solution to be tested is added to one test tube, and an equal volume of water is added to the other. In the presence of starch, the blue color is apt to obscure the brown tint produced by the erythro-dextrin. This may be avoided to some extent by employing the iodine solution somewhat in excess, so as to get a full development of the brown color.

Pure dextrin is a white amorphous solid. It is tasteless and odorless and nonvolatile. It is·very deliquescent and dissolves in an equal weight of cold water to form a syrupy and strong dextrorotary liquid which is miscible with one and one-half times its volume of 50 per cent. ethyl alcohol. By the addition of 95 per cent. alcohol, if used in sufficient quantity, dextrin is completely separated from its aqueous solution. Cold concentrated sulphuric acid dissolves dry dextrin without color, but charring takes place on warming. By boiling with dilute acids, dextrin yields maltose and ultimately dextrose. Hot nitric acid of specific gravity 1.35 converts dextrin in part to oxalic acid, whereas the natural gums yield mucic acid under similar conditions.

Dextrin is distinguished from starch by its solubility in cold water; it is differentiated from soluble starch by yielding no blue color with iodine, and no precipitate with baryta water; it is distinguished from maltose and dextrose by not reducing Fehling's solution; it is distinguished from gelatine and egg albumen by not yielding a precipitate with tannin; from albumen by not being coagulated by heat or mineral acids.

Dextrin is separated from starch and cellulose by solution in cold water; coagulable albuminoids may then be separated by raising the solution, made faintly acid, to boiling. An ammoniacal solution of acetate of lead added to the cold and dilute liquid will precipitate the dextrin and leave the sugar in solution. The precipitate may be dried at 100° C. Another method consists in precipitating the dextrin by means of a large proportion of alcohol and washing the precipitate with rectified spirits and drying it at 110° C. After weighing, the dextrin should be ignited and the resultant ash deducted from the total weight obtained.

Unaltered starch in dextrin may be recognized by the microscope, and by its insolubility in cold water. Reducing sugars are nearly always present in commercial dextrin and may be detected and estimated by Fehling's solution. Many mixtures of starch and dextrin are employed as thickening agents in calico-printing. An example of such a compound is the product known as "Gloy," which consists essentially of farina mixed with a solution of magnesium chloride. Dextrin sirups are largely employed by confectioners. Dextrin may be distinguished and separated from gum arabic by means of ferric chloride, which precipitates the latter only.

SPECIFICATIONS.

After considerable preliminary investigation of commercial dextrin with a view of making specifications that should be suitable for the dextrin in pyrotechnic use, it developed that the most suitable and satisfactory method of procedure would be not to set specifications giving the percentage of impurities, etc., nor to make any requirements, nor set limitations, other than by specifying the dextrin employed in pyrotechnic compositions by the manufacturers of fireworks and pyrotechnic pieces at the present time. The commercial varieties are so well known and so well standardized that it is deemed advisable to make the specifications for dextrin consist only of the statement of the grade. The grade commonly used in pyrotechnic compositions by firework manufacturers is known as No. 152, which is an unrefined product. This article is in appearance a very light-brown, dry powder, of the consistency of wheat flour.

CHAPTER XIV.

ANTIMONY SULPHIDE.

HISTORY.

The antimony in antimony sulphide belongs to the same natural family of the elements as nitrogen, phosphorus, arsenic, and bismuth. Antimony, in the form of its sulphide, has been known from very early times, more especially in eastern countries, reference being made to it in the Old Testament. The Arabic name for the naturally occurring stibnite, which is the mineral term for antimony sulphide, is "Kohl"; Dioscoridès mentions it under the term "Stimmi"; Pliny as "Stibium"; Geber as "Antimonium." Early German writers called it "Speissglanz." Basil Valentine alludes to it in his "Triumphal Car of Antimony" in about the year 1600, and at a later date he describes the preparation of the metal.

Another form of the metal, known as explosive antimony, was discovered by Gore in 1857, on electrolyzing a solution of antimony trichloride in hydrochloride acid, using a positive pole of antimony and a negative pole of copper or platinum. This form of antimony has a specific gravity of 5.78 and always contains some unaltered antimony thichloride. It is very unstable, a scratch causing it instantaneously to pass into the stable form with explosive violence and the development of much heat.

As far back as the time of Basil Valentine and Paracelsus, antimonial preparations were in great vogue as medicinal agents, and came to be so much abused that a prohibition was placed upon their employment by the Paris Parliament in 1566. Metallic antimony was utilized to make goblets in which wine was allowed to stand so as to acquire emetic properties, and "everlasting" or "family" pills of the metal, supposed to act by contact merely, were administered, and recovered for future use after they had fulfilled their purpose.

105

TOXICOLOGY.

Antimony is one of the poisons, directly lethal to all living matter. In acute poisoning by it, the symptoms are almost identical with those of arsenical poisoning, which is much commoner. The post-mortem appearances are also very similar, but the gastro-intestinal irritation is much less marked, and inflamation of the lungs is more commonly seen. Chronic poisoning by antimony is very rare, but resembles in essentials chronic poisoning by arsenic. In its medico-legal aspects antimonial poisoning is of little and lessening importance.

Tartar emetic, which is antimony tartrate, when swallowed acts directly on the walls of the stomach, producing vomiting, and after absorption continues this effect by its action on the medulla. It is a powerful cardiac depressant, diminishing both the force and frequency of the heartbeat. It depresses respiration, and in large doses lowers temperature. It depresses the nervous system, especially the spinal cord. It is carried off by all the secretions and excretions of the body. On the skin, its action is that of a diaphoretic, and being also excreted by the bile, it acts slightly as a cholagogue. Summed up, its action is that of an irritant and a cardiac or nervous depressant.

OCCURRENCE IN NATURE.

Antimony occurs in nature most abundantly as antimony sulphide in the mineral stibnite. Another form of antimony sulphide found is the mineral kermesite. It also occurs as the metal and as the oxide in the minerals valentinite and senarmontite. Antimony is frequently found associated with lead. Of the minerals of antimony, the most important commercially are the sulphides. The chief producing countries of antimony sulphide at the present time are France, Italy, Mexico, and Japan. It is also found in China and South America. Metallic antimony found in nature is sometimes associated with arsenic, iron, and silver. It is tin white in color, very brittle, usually massive, with fine granulated steel-like texture, or lamellate or radiate in structure. It is very rarely found in rhombohedral crystals or complex

groups. It has a specific gravity of 6.65 to 6.72 and a hardness of 3 to 3.5. It fuses easily and colors the flame green, giving copious white fumes which continue to form as a thick cloud after cessation of the blast from a blowpipe. It often yields a crust of needlelike crystals.

Stibnite, the most important of the antimony minerals, when pure, contains 71.4 per cent. antimony and 28.6 per cent. sulphur. It sometimes contains silver and gold. It is a lead-gray mineral of bright metallic luster, occurring in imperfectly crystallized masses with a columnar or bladed structure; less frequently it is found in distinct prismatic orthorhombic crystals, or confusedly interlaced bunches of needlelike forms, and in granular compact masses. It differs from galenite in cleavage, and from all sulphides by the ease with which it fuses and the cloudlike fumes given off. It occurs in veins with other antimony minerals formed from it by the action of air and water, and also with cinnabar, sphalerite, siderite, etc.

Large deposits of stibnite occur at Lovelocks, Bernier, and Austin, Nev.; at Kingston, Idaho; at San Emidio, Calif.; in Arkansas; in Utah; in Nova Scotia, and in New South Wales. The most celebrated deposit, however, is that in Shikoku, Japan, from which the very finest crystals and groups are obtained.

The mineral kermesite, known as red antimony, has the formula Sb_2S_2O. When pure, it contains 75 per cent. antimony, 20 per cent. sulphur, and 5 per cent. oxygen. It occurs in fine hairlike tufts or radiating fibers and needlelike crystals of a deep cherry-red color and almost metallic luster. It is nearly opaque. It gives a bright-red streak. It has a hardness of 1 to 1.5 and a specific gravity of 4.5 to 4.6. It is sectile, and in thin leaves it is slightly flexible. This mineral results from the partial oxidation of stibnite. Extensive deposits at Pereta, Tuscany.

The mineral senarmontite, having the formula Sb_2O_3, contains 83.3 per cent. antimony when pure. It is colorless to gray and occurs in octahedral crystals and granular masses. It is transparent to translucent and has a resinous luster. It has a specific gravity of 5.22 to 5.3 and a hardness of 2 to 2.5. Before the blowpipe, this mineral fuses easily, coating the charcoal with the white oxide of antimony. In the reducing

flame, metallic antimony is produced, which in the oxidizing flame again forms the oxide, coloring the flame green. It is formed by the oxidation and decomposition of stibnite and other ores of antimony. It is soluble in hydrochloric acid.

Another form of the oxide of antimony found in nature is the mineral valentinite, which also has the formula Sb_2O_3 and when pure contains 83.3 per cent. of antimony. This mineral occurs in small white flat crystals of the orthorhombic system, or in fan-shaped groups of a somewhat silky luster, and white or gray in color. It is also found in spheroidal masses with radiating lamellar structure. It is translucent and has an adamantine or silky luster. It is white or gray, or pale red in color; it has a hardness of 2.5 to 3 and a specific gravity of 5.7. The behavior of this mineral before the blowpipe is the same as that of senarmontite.

METHOD OF MANUFACTURE.

The antimony sulphide, which is used in pyrotechnic compositions, is nothing more than the mineral stibnite in as pure a grade as can be obtained, ground to the required fineness. In some countries, however, where the stibnite occurs associated with considerable quantities of gangue, it is purified by the process known as " liquation." The ore containing the stibnite is heated and the mineral melts, forming a comparatively thin liquid which is drawn off into suitable receptacles. On cooling, it solidifies, and is shipped in this form. A product relatively free from gangue is thus obtained and the freight on useless material is saved. This liquated product may be ground and used in the same way as stibnite.

Artificial antimony is prepared by four methods:

1. Thirteen parts of pure antimony are mixed with 5 parts of flour of sulphur and projected in portions into a red-hot crucible; when completely fused, it is poured out and any free metal is detached from the mass. The product is antimony sulphide, which is then ground and ready for use. During this process any oxide of antimony, which might be contained in the mineral, will be converted into sulphide.

2. Hydrogen sulphide precipitates antimony sulphide as an orange precipitate from a solution of any antimony salt.

This precipitate when washed and dried is a pure antimony sulphide.

3. Digest for two hours in a closed vessel, 1 part of crude antimony sulphide, 1 part of pearl ash, 1.5 parts of lime, and 15 parts of water; when sulphuric acid is added to the extract the alkaline sulpho-salt first formed is decomposed with the precipitation of the sulphide. When washed and dried a pure antimony sulphide is produced.

4. The fourth method consists in the precipitation in the sulphide of antimony from solutions of antimony salts by sodium thiosulphate, $Na_2S_2O_3$. This results in the formation of a precipitate containing both antimony sulphide and sulphur, and as sulphur is used in pyrotechnic compositions in connection with antimony sulphide, the precipitate containing both these substances might be very appropriate for pyrotechnic use.

AVAILABILITY OF SUPPLY.

During 1917, antimony was mined in China, Japan, Bolivia, France, Italy, Mexico, the United States, Africa, Australia, Spain, and Canada. No doubt it was also mined in Germany and Hungary, both of which countries contain supplies of the ore, especially the latter. No data, however, are available at this time as to its production during the war.

In Mineral Industry for 1917, the following figures are given for antimony and its ores in the United States for 1915:

[Short tons.]

Sb in domestic ores	2,100
Sb in antimonial lead of domestic origin	2,000
Sb in antimonial lead of foreign origin	464
Sb recovered from scrap alloys	3,102
Sb smelted from imported ore	1,687

Exports of ore from Alaska in 1916 were 1,390 tons carrying about 57 per cent. Sb.

PRODUCTION IN OTHER COUNTRIES.

Exports of antimony regulus from Shanghai during 1917.

Destination.	Jan.	Feb.	Mar.	Apr.	May.	June.	July.	Aug.	Sept.	Oct.	Nov.	Dec.	Total.
													Tons.
New York	210	308	512	250	295	1,035	650	260	700	271	799	350	5,642
San Francisco		625				100		50			25		800
Vancouver			200	600	600	250	650	200			1		2,500
Montreal			20										20
London	100	200	50		10	55	55	45	55	38	25		633
Liverpool								5		60	25		90
Genoa					520							200	720
Marseilles	20				100								120
Vladivostok		400									405		805
Osaka	71	70			50	100				50	75	30	446
Kobe	50	50	5			190	565	74	250		100	200	1,484
Yokohama						50					50		100
Moji										40			40
Hongkong								50	50			150	250
Semarang									7				7
Total	451	1,653	787	850	1,575	1,780	1,920	684	1,062	459	1,504	930	13,657

Exports of antimony crude from Shanghai during 1917.

Destination.	Jan.	Feb.	Mar.	Apr.	May.	June.	July.	Aug.	Sept.	Oct.	Nov	Dec.	Total.
													Tons.
New York	100	195	809	50	425	547	100		49				2,275
San Francisco		50											50
Vancouver					655								655
Montreal													
London	179		64	950	310		20	610	50		50		2,233
Liverpool												10	10
Genoa					30								30
Marseilles	50			265						30			345
Vladivostok													
Osaka	485	250	1,043	1,313	1,207	994	568	720	270		50		690
Kobe	100	383	355	937	1,229	1,798	1,213	379	100	30	150	150	6,824
Yokohama			100	100	300	560	260		100		50		1,470
Moji													
Hongkong													
Baravia												1	1
Surabaya												5	5
Tokyo			10										10
Total	914	878	2,381	3,615	4,156	3,899	2,161	1,709	569	60	300	166	20,808

Production of antimony metal in foreign countries.

[In metric tons.]

	1905	1906	1907	1908	1909	1910
Austria	90		207	162		
China[1]	3,333	3,829	2,316	9,356	7,937	6,643
France	2,396	3,433	3,945	3,850	5,444	4,640
Hungary[2]	756	1,322	841	670	695	782
Italy	327	537	610	345	59	
Japan	190	627	248	198	157	120

	1911	1912	1913	1914	1915	1916
Austria		13				
China[1]	6,986	13,531	13,032	19,645	23,357	24,727
France	4,775	5,406	6,390			
Hungary[2]	892	859	1,038			
Italy			76	138	481	4,334
Japan	97	80	21	3,865	8,347	12,396

[1] Exports of regulus and refined metal. [2] Regulus.

Imports of antimony into the United States according to the Bureau of Foreign and Domestic Commerce.

[In pounds.]

Month.	1916		1917	
	Ore.	Regulus, matte, or metal.	Ore.	Regulus, matte, or metal.
January	660,309	89,600	818,717	1,217,312
February	448,684	2,246,623	319,945	1,007,600
March	803,097	1,202,150	914,783	123,000
April	982,851	2,984,600	440,792	1,727,426
May	1,933,472	2,642,560	2,385,975	5,123,971
June	1,755,817	4,980,751	1,855,584	2,815,235
July	1,505,812	380,800	1,442,929	2,856,333
August	596,979	3,414,693	1,457,798	6,414,175
September	47,315	342,185	1,475,335	5,609,906
October	520,051	....	227,329	3,518,968
November	163,726	941,548	425,108	2,619,132
December	67,310	544,320	156,148	2,615,855
Total	9,485,423	19,749,830	11,920,443	35,649,113

Antimony statistics of the United States.

[In tons of 2,000 pounds.]

Year.	Imports antimony content.				Production.[1]		
					In hard lead.		Recovered from old alloys scrap, dross, etc.
	Metal regulus.	Crude and ore.	Type metal.	From domestic ore.	From domestic ore.	Imported ore.	
1906	3,950	1,124	1,853	404	1,362	....	....
1907	4,331	1,380	1,369	351	1,561	....	....
1908	4,057	1,640	422	....	2,246	....	....
1909	4,826	1,693	1,327	....	1,617	743	1,556
1910	4,950	....	1,109	....	1,598	631	2,779
1911	5,479	....	727	....	1,543	711	2,359
1912	6,969	25	52	....	1,224	725	2,506
1913	7,667	993	50	....	2,204	304	2,705
1914	6,535	993	94	....	2,530	175	2,645
1915	8,747	[2] 1,682	....	....	5,364	1,687	3,102
1916	9,875	[2] 4,742	....	....	1,770	....	4,480
1917	17,825	[2] 5,960	....	....	....	....	....

[1] Figures of United States Geological Survey.   [2] Ore only.

Yearly imports of antimony metal and ore from 1900 to 1917 into the United States.

Year.	Metal.	Crude and ore.	Year.	Metal.	Crude and ore.
1900	3,654,822	6,089,132	1909	9,557,956	3,453,542
1901	3,640,505	1,682,301	1910	7,955,945	1,346,962
1902	5,388,739	3,129,069	1911	8,486,137	1,641,467
1903	4,694,309	2,714,617	1912	13,936,873	1,562,066
1904	4,268,045	2,488,518	1913	12,479,727	4,021,486
1905	4,941,247	1,970,788	1914	13,110,426	2,606,349
1906	10,305,734	1,972,658	1915	17,484,030	3,374,012
1907	9,600,901	2,771,387	1916	19,749,830	9,485,423
1908	8,089,915	3,287,218	1917	35,649,113	11,920,443

The increased imports into the United States during 1917 came principally from Japan. This country has evidently taken advantage of the situation in China to secure for herself an adequate supply of antimony ore, and it is really amazing to observe the large number of Japanese concerns that are interested in antimony. It was known that previous to the Russian Revolution Japan had come to some agreement with Russia for the supply of war munitions and raw materials. When Russia ceased to be an effective force in the war, the Japanese were forced to find a new outlet for their large stores of antimony. The needs of the European Allies were already well covered, and, consequently, the surplus found its way to the United States of America.

The total imports were roughly 70 per cent. greater in 1917 than in 1916, but as the price ruled much lower the total value of the imports was nearly $1,000,000 less than for the previous year.

The exports of antimony from the United States during the year amounted to only 989,477 pounds, as compared with 3,273,946 during 1916. This was due to the fact that the Canadian Government adopted the sensible plan of importing direct from producers. In this way their supply of antimony was assured and they had no cause to worry over the movements of the market.

USES OTHER THAN IN PYROTECHNICS.

The most important use of antimony sulphide is as the source of metallic antimony, which occupies a very important position in the arts. Its use as an artificial pigment is of considerable importance and it is also used in pharmaceutical preparations. In the natural state, antimony sulphide is used in safety matches, percussion caps, and rubber goods. It is a specific in medicine for scrofula, chronic rheumatism, and cutaneous diseases. In addition, it is used as an emetic and an expectorant.

Antimony sulphide is used to a slight extent in vulcanizing rubber. It has been used to form part of the powder composition for shrapnel shells required to produce a dense cloud of white smoke on bursting. Antimony sulphide is used in making Swedish safety and wax matches, as well as in the composition on the side of the box on which the

matches are ignited. The heads of the match contain about 3 per cent. of the trisulphide of antimony, while the composition on the box contains about 8 per cent. of the same material. For this purpose the native antimony sulphide is used by the match manufacturers.

As a pigment, artificial antimony sulphide is in many ways superior to red oxide of lead, chromate of lead, or mercury vermilion.

Antimony yellow is produced by the slow oxidation of the sulphide. Various shades of yellow are formed by mixing it with red lead and zinc white. Antimony blue, etc., or other pigments are produced by mixtures of the foregoing with other mineral compounds. The pentasulphide of antimony formed by a fusion of the red trisulphide of antimony with sulphur is used as the vulcanizer for the insulation of electric cables. In the vulcanizing process, this powder parts with the excess of its sulphur content and is again reduced to the trisulphide. The latter mixes mechanically with the rubber, giving a red color.

In enameling processes and in glass-staining, antimony tetroxide, which has the formula Sb_2O_4, is mixed with white lead and borax to produce a yellow color. A white enamel is now made with trioxide, this compound to some extent replacing tin oxide.

The value of stibnite is principally as the source of metallic antimony, and this makes it desirable that the uses of antimony metal be briefly considered.

Britannia metal is an alloy of antimony, tin and lead, and is largely used in the manufacture of spoons, teapots, etc.

Babbitt metal is generally tin, antimony, and copper.

Type metal is lead, antimony, and tin.

Shrapnel lead carries from 12 to 25 per cent. of antimony. Hard lead carries from 5 to 7 per cent. of antimony and has a great variety of uses. It is alloyed with lead in storage batteries and accumulators. It is used as a substitute for tin in electric cables, on account of its lower price. With lead it is also used in the manufacture of toys, photograph frames, and other bric-à-brac.

The uses of antimony compounds are discussed in detail by Mr. B. Dunstan, chief Government geologist of Queensland,

Australia, in a pamphlet published by the Queensland Government Mining Journal of February 15, 1917.

The substitution of antimony for tin, on account of its lower price, is being investigated at the present time. The supply is capable of meeting a large demand, and the cheapness of the metal will no doubt attract its more extended use in the arts in the near future.

PHYSICAL PROPERTIES.

Color and odor.—The antimony sulphide used in pyrotechnic compositions is the black mineral, stibnite, which has been ground to a powder. It has a lead-gray color, often black with an iridescent tarnish, a metallic luster and lead-gray streak. It cleaves easily in planes parallel to the brachypinacoid, yielding slightly flexible bladelike stripes.

Solubility.—One hundred parts of cold water dissolve 0.000175 parts, and in hot water antimony sulphide decomposes.

Hygroscopicity.—The substance is not hygroscopic, but on exposure to moist air it undergoes a very slow oxidation.

Flame color.—It imparts a green color to the flame which is characteristic of antimony salts.

Fusibility.—It melts at 546° C. and rapidly volatilizes at and above that temperature.

Hardness.—It has a hardness of 2, which is about the hardness of gypsum, and is therefore very soft and easily ground.

CHEMICAL PROPERTIES.

GENERAL NATURE.

The molecular weight of antimony sulphide is 336.58. This is made up of two atoms of antimony with a combined weight of 240.40 and three atoms of sulphur with a combined weight of 96.18. It has the formula Sb_2S_3. It carries no water of crystallization.

REACTIONS.

The native antimony sulphide is decomposed by concentrated hydrochloric acid, forming a clear solution of antimony chloride with the evolution of hydrogen sulphide. On

the addition of water a white basic salt is precipitated, which after further dilution and the addition of hydrogen sulphide forms antimony sulphide again as an orange precipitate. Strong nitric acid decomposes stibnite into the white pentoxide and sulphur. A strong hot solution of caustic potash colors stibnite yellow and partially dissolves it. If hydrochloric acid is added to such a solution the characteristic orange precipitate of antimony sulphide comes down.

FUNCTION IN PYROTECHNIC PIECES.

The function of antimony sulphide, in the pyrotechnic compositions in which it is used, is that of a reducer, as both the antimony and sulphur contained combine with active oxygen, forming oxide of antimony and oxides of sulphur. It is used in the first-fire composition for position lights and smoke torches. In the former the antimony composition contains saltpeter 56.5 per cent., arsenic disulphide 9.4 per cent., antimony sulphide 9.4 per cent., flour of sulphur 18.8 per cent., dextrine 5.9 per cent.; while the latter composition contains saltpeter 63 per cent., flour of sulphur 15.8 per cent., antimony sulphide 10.6 per cent., meal powder 10.6 per cent.

As antimony does not give any intense characteristic color to the flame, the function of its sulphide is simply that of a reducer, or as fuel for the fire, and during its oxidation by the active oxygen of the saltpeter a very large amount of heat is liberated.

METHOD OF ANALYSIS.

The following methods for the analysis of antimony sulphide are based on the assumption that it is the reasonably pure stibnite, which is known as the powdered gray antimony or stibnite of commerce.

QUALITATIVE TESTS.

Qualitative tests are not recommended in the investigation of this substance, as little can be learned concerning its composition without going through as many operations as would be required for a quantitative investigation.

QUANTITATIVE TESTS.

Moisture.—A weighed sample of 3 grams shall be spread out on a 3-inch watch glass and dried in an air bath at 110° C. to constant weight. The loss in weight thus determined represents the amount of moisture present. This loss in weight, divided by the weight of the sample taken, gives the percentage of moisture.

Antimony.—Three-tenths gram of the sample shall be accurately weighed and carefully transferred to a 800 c. c. Erlenmeyer flask. Thirty-five cubic centimeters of concentrated hydrochloric acid of a specific gravity of 1.19 shall be added and the solution allowed to stand in the cold for 30 minutes. The flask shall then be heated on the water bath to expel the hydrogen sulphide. Twenty cubic centimeters of concentrated hydrochloric acid, 20 c. c. of concentrated sulphuric acid, and 100 c. c. of water shall be added and the solution boiled from 15 to 20 minutes to drive off all the SO_2 and H_2S which shall have been formed. The solution shall then be diluted to about 600 c. c. and the flask corked to avoid unnecessary contact with the air. The solution shall then be cooled quickly under the tap. When cool, the solution shall be titrated with one-tenth normal potassium permanganate, which has been standardized against Sorenson's sodium oxalate, or against C. P. metallic antimony, to the first permanent pink tinge. The reaction which takes place between the $KMnO_4$ and the antimony chloride is as follows: $5SbCl_3 + 2KMnO_4 + 10HCl + 3H_2SO_4 = 5SbCl_5 + K_2SO_4 + 2MnSO_4 + 8H_2O$; therefore, $SbCl_3$ is equivalent to O or Sb to one atom of oxygen.

The atomic weight of antimony is 120.2 and that of oxygen 16; consequently, the weight of oxygen consumed in the titration by the potassium permanganate, multiplied by the fraction $\frac{120.2}{16}$, or 7.5125, will give the weight of antimony in the sample, and this weight, divided by the weight taken, will give the percentage of antimony.

Acidity.—A sample of about 10 grams shall be treated with 100 c. c. of neutral distilled water and heated quickly to boiling while being stirred. The solution shall then be filtered and tested with delicate neutral litmus paper. It shall show no acid reaction at the end of 10 minutes.

Insoluble matter.—Five grams of the sample shall be treated with 200 c. c. of aqua regia (1 part of nitric acid to 3 parts of hydrochloric acid) in a 400 c. c. beaker, and heated on a hot plate for half an hour to complete the solution and expel the gases formed. The solution shall then be filtered on a well-packed asbestos Gooch crucible which has been previously weighed, and the residue shall be washed with 10 c. c. of concentrated hydrochloric acid, followed by hot water, and one treatment with acetone. The residue in the crucible shall be dried at 150° C., and finally ignited to volatilize any separated sulphur. The crucible shall be placed in a desiccator, allowed to cool, and then weighed. This residue shall be reported as matter insoluble in aqua regia. It consists principally of silica. The weight of the residue divided by the weight taken will give the percentage of matter insoluble in aqua regia in the sample.

Sulphur.—Five-tenths gram of the powdered sample shall be placed in a covered No. 2 beaker, to which shall be added 1 c. c. of water, 9 c. c. of glacial acetic acid, and 6 c. c. of liquid bromine. The solution shall be allowed to stand overnight at room temperature. In the morning 20 c. c. of concentrated hydrochloric acid shall be added and the solution warmed gently for half an hour. The watch glass shall then be removed, and the solution evaporated nearly to dryness on a steam bath under a hood. Ten cubic centimeters of concentrated hydrochloric acid and 150 c. c. of hot water shall then be added. To the warm solution 0.5 gram of powdered aluminum shall be added a little at a time, and the solution stirred until the antimony is precipitated as the metal; this operation should take about 20 minutes. The solution shall then be filtered and the precipitate washed with hot water. The filtrate shall be allowed to cool, diluted to 400 c. c., and brought to boiling. Twenty-five cubic centimeters of a previously heated 10 per cent. solution of barium chloride shall be added, and the solution boiled for a few minutes. The solution carrying the precipitate of barium sulphate shall be allowed to stand on the hot plate until it is clear; it shall then be filtered through ashless paper and thoroughly washed with hot water until free from chlorides. The precipitate and paper shall then be transferred to a previously weighed platinum crucible and ignited with the

full flame of a Bunsen burner, and placed in a desiccator and allowed to cool. It shall then be weighed.

One molecule of barium sulphate having the formula $BaSO_4$ is equivalent to one atom of sulphur, consequently, to obtain the factor by which to multiply the weight of barium sulphate, in order to get the weight of the sulphur content, the atomic weight of sulphur, 32.06, shall be divided by the molecular weight of barium sulphate, 233.43. This gives 0.1373, and the weight of barium sulphate obtained multiplied by this factor will give the weight of sulphur in the sample taken; and this weight divided by the weight of the sample will give the percentage of sulphur.

The reactions represented by the operations described above are as follows:

$$Sb_2S_3+12H_2O+28Br=2SbBr_5+3H_2SO_4+18HBr.$$

Of course, there may be an interaction between the bromide of antimony and sulphuric acid, but for the purpose of expressing the oxidation which takes place the reaction as outlined is sufficient.

During the reduction with the aluminum the reaction takes place as follows:

$$6SbBr_5+15H_2SO_4+10Al=6Sb+30HBr+5Al_2(SO_4)_3.$$
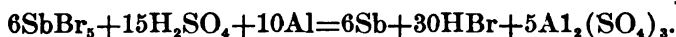
Finally, when the barium sulphate is precipitated, it is according to the reaction:

$$BaCl_2+H_2SO_4=BaSO_4+2HCl.$$
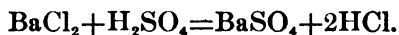
Antimonous oxide.—Antimonous oxide shall be determined by computing the amount of antimony sulphide present in the sample from the sulphur content as determined in one of the preceding tests. The amount of antimony found in excess of that combined as sulphide shall be calculated to the oxide and reported as antimonous oxide. The calculations to accomplish this are as follows:

The molecular weight of antimony sulphide is 336.58.

The total atomic weight of its sulphur content is 96.18. Dividing 336.58 by 96.18, we obtain the factor 3.4995. The weight of sulphur found in the sample when multiplied by

this factor will give the weight of antimony sulphide in the sample, and this weight, divided by the weight taken, will give the percentage of antimony sulphide.

The molecular weight of antimony sulphide is 336.58.

The total atomic weight of its antimony content is 240.4, so that, dividing 240.4 by 336.58, we shall obtain the factor 0.7142; therefore, the weight of antimony sulphide as above calculated, multiplied by this factor 0.7142, will give the weight of antimony which is combined as the sulphide in the sample. If this weight of antimony is deducted from the total amount of antimony in the sample as previously determined, the difference will be the amount of antimony which exists in the sample in the form of the oxide Sb_2O_3.

The molecular weight of antimonous oxide, Sb_2O_3, is 288.4. The total atomic weight of its antimony content is 240.4; consequently if the weight of antimony in excess of that contained as the sulphide be multiplied by the fraction $\frac{288.4}{240.4}$ or 1.20, the weight of the antimonous oxide, Sb_2O_3, in the sample, will be obtained, and this weight, divided by the weight of the sample, will give the percentage of the oxide.

Arsenic.—It is not infrequent to find arsenic in the ground mineral stibnite, and it is therefore necessary to make a determination for arsenic, which, if found, must be calculated to correct for the amount of $KMnO_4$ which it would consume in the titration in the determination of antimony in the sample.

Two grams of the sample shall be mixed in a good-sized porcelain crucible with 10 grams of a mixture of equal parts of sodium carbonate and potassium nitrate. The crucible shall then be heated over a Bunsen burner very gradually, until the contents are brought to a state of fusion. The state of fusion shall be maintained for 10 minutes. The contents of the crucible shall then be poured out on an iron plate. When cool, they shall be disintegrated in hot water, the insoluble matter filtered off, and the residue washed with hot water. The arsenic will now be present in the solution in the form of sodium arsenate, while the antimony will be in the insoluble residue. The filtrate shall be acidified with nitric acid and boiled until the carbonic acid has been driven off. An excess of an emulsion of zinc oxide shall then be added and should an unusual heavy precipitate be produced, the solution shall be filtered, the residue washed and the filtrate again treated

with the emulsion of zinc oxide. This thorough treatment with zinc oxide is necessary to obtain the perfectly neutral solution which is essential for the next operation.

To the clear filtrate from the zinc-oxide silver-nitrate solution shall be added in slight excess, accompanied by vigorous stirring.

Traces of arsenic will be indicated by the darkening of the solution. If appreciable quantities of arsenic are present, it will be indicated by a reddish-brown precipitate of silver arsenate, which has the formula Ag_3AsO_4. This shall be treated in the following manner:

After stirring the solution carrying the precipitate of silver arsenate, it shall be filtered and the precipitate washed with cold water. In order to determine whether the precipitation of silver arsenate has been complete or not, the filtrate shall be treated with a solution of silver nitrate which has been rendered slightly alkaline with ammonia. If a precipitate is formed, it is an indication that sufficient silver nitrate was not used to precipitate all as silver arsenate, or that the process of neutralizing by zinc oxide was not complete. In either event, the determination should be begun again, correcting the procedure for whichever condition was found to be the cause of the incomplete precipitation. After it has been determined that the precipitation of silver arsenate is complete, the precipitate shall be dissolved in 10 c. c. of strong acetic acid and boiled under a hood. The solution shall be allowed to cool, and three drops of phenolphthalein shall be added and sufficient caustic soda to render the solution alkaline. Dilute acetic acid shall then be added drop by drop until the purple color is discharged, followed by 5 c. c. of a 10 per cent. solution of ferric alum.

For the completion of the determination two standard solutions are required. First: A standard solution of silver nitrate prepared by dissolving 17 grams of the pure crystalline salt in 1,000 c. c. of water. Second: A solution of potassium thiocyanate prepared by dissolving about 10 grams of the salt in 1,000 c. c. of water.

Of these two solutions the silver nitrate shall be regarded as the standard, and the relative strength of the potassium-thiocyanate solution shall be determined by titrating a known volume of the silver-nitrate solution, to which 5 c. c.

of a 10 per cent. solution of ferric alum has been added with the potassium thiocyanate solution, until the appearance of the red color of the ferric thiocyanate indicates that the silver has all been precipitated as the thiocyanate. From the results of the titration the silver-nitrate equivalent of 1 c. c. of the thiocyanate solution shall be calculated.

The acetic acid solution of the silver arsenate shall now be titrated with the potassium-thiocyanate solution as above standardized. From the volume of the thiocyanate solution required the equivalent amount of silver nitrate shall now be calculated.

Three molecules of silver nitrate are equivalent to 1 molecule of silver arsenate, which is equivalent to 1 atom of arsenic. These 3 molecles of silver nitrate have the combined molecular weight of 509.67, while arsenic has the atomic weight of 74.96, consequently the weight of silver nitrate to which the thiocyanate solution used is equivalent, multiplied by the fraction $\frac{74.96}{509.67}$ or 0.1471 will give the weight of arsenic in the sample, and this weight divided by the weight taken, will give the percentage of arsenic.

The following results were obtained from the quantitative tests made upon a sample of antimony sulphide received from one of the pyrotechnic manufacturers.

Moisture:

	Grams.
Weight taken	0.3
Weight after drying	2.9979
Loss in weight	.0021

This divided by the weight taken gives 0.07 per cent.

Antimony:

	Grams.
Weight taken	3
Number of cubic centimeters of permanganate used	35.6

1 c. c. $KMnO_4$ used=0.0008 gram active oxygen. This 35.6 c. c. $KMnO_4$ contains 0.0285 gram active oxygen; this weight multiplied by the factor 7.5125 gives 0.2141 gram as the weight of the antimony content of the sample. This weight divided by the weight taken gives 71.37 per cent. of antimony.

Acidity: Neutral.

Insoluble matter:

	Grams.
Weight taken	5
Weight of insoluble matter	.1988

This weight, divided by the weight taken, equals 3.98 per cent.

Sulphur:
                                                          Gram.
Weight taken_____ 0. 5
Weight barium sulphate_____ . 7359

This weight multiplied by the factor 0.1373 gives 0.10104 gram sulphur. This weight, divided by the weight taken, gives 20.21 per cent.

Antimony sulphide: Weight of sulphur contained in 1 gram of the sample=0.2021 gram. This weight multiplied by the factor 3.4995 gives 0.7072 gram as the weight of antimony sulphide in the sample; this is equivalent to 70.72 per cent.

Antimonus oxide: Weight of antimony sulphide in 1 gram sample=0.7072 gram. This multiplied by the factor 0.7142 gives 0.5051 gram of antimony in antimony sulphide. By subtracting the weight of antimony in antimony sulphide from the weight of total antimony obtained, 0.7137 gram, we obtain the weight 0.2086 gram, which is equal to the weight of antimony in excess of that required to combine with the sulphur. This weight multiplied by the factor 1.2 gives 0.2504 gram of Sb_2O_3 in 1 gram of the sample, which is equal to 25.04 per cent.

Arsenic: Absent.

The above results are tabulated as follows:
                                                        Per cent.
Moisture _____ 0. 07
Sb_2S_3 _____ 70. 72
Insoluble matter _____ 3. 98
Sb_2O_3 _____ 25. 04
                                                       ———————
          Total_____ 99. 81

SPECIFICATIONS.

The following specifications are based upon the native commercial antimony sulphide from which the above sample was prepared:

No. 1. The material shall be the crystalline native-occurring variety of shining needlelike structure and steel gray in color, or liquated Chinese or Japanese (crude) or (needle) antimony sulphide. If supplied in lump form, it shall be clear and free from adhering gangue material or scale. The ground sul-

phide of antimony shall be free from dirt, sticks, and other foreign material.

No. 2. The material shall contain not less than 70 per cent. of antimony sulphide calculated from the sulphur content obtained by analysis.

No. 3. The material shall contain not more than 25 per cent. of antimonous oxide Sb_2O_3 calculated from the excess of antimony present over that required to combine with the sulphur.

No. 4. The material shall contain not more than 4 per cent. of matter insoluble in aqua regia.

No. 5. The material shall be free from acidity.

No. 6. The material shall not contain more than 0.25 per cent. moisture when compounded.

No. 7. Before use the material shall be ground so that all shall pass through a 60-mesh sieve and at least 60 per cent. shall pass through a 100-mesh sieve.

DISCUSSION OF SPECIFICATIONS.

In presenting the above specifications it must be borne in mind that antimony sulphide, unlike many of the other compounds used in pyrotechnic compositions, is a native-occurring material, and a greater latitude must be permitted in setting specifications for material which would be acceptable in pyrotechnic compositions on this account. The presence of a certain amount of gangue and of the antimonous oxide, which is an oxidation product of the antimony sulphide naturally occurring in the mineral, is not to be avoided, as these impurities are invariably found in the purest mineral available.

In the specifications above set forth great latitude is given as regards the amount of these materials which are permissible in order that the native mineral from many localities may be used in the pyrotechnic compositions.

At the present time sulphide of antimony is only used in smoke-torch first-fire composition. This composition is made up in the form of a paste and is not subjected to compression, consequently the sand and grit from the gangue of the native mineral do not contribute a source of danger, which would be the case if the composition was made by compression. Practically the only requirements of the sulphide of antimony are those of a " fuel for the fire " and almost any clean crystalline native-occurring sulphide of antimony, or a liquated product therefrom, will be found acceptable in

pyrotechnic use for the particular composition in which it now enters. Should future developments require a sulphide of antimony for compositions to be subjected to compression, for example, it might be necessary to require a different grade of material for them and a precipitated sulphide of antimony might be required.

International atomic weights, 1917.

	Symbol.	Atomic weight.		Symbol.	Atomic weight.
Aluminum	Al	27.1	Neodymium	Nd	144.3
Antimony	Sb	120.2	Neon	Ne	20.2
Argon	A	39.88	Nickel	Ni	58.68
Arsenic	As	74.96	Niton (radium emana-		
Barium	Ba	137.37	tion)	Nt	222.4
Bismuth	Bi	208.0	Nitrogen	N	14.01
Boron	B	11.0	Osmium	Os	190.9
Bromin	Br	79.92	Oxygen	O	16.00
Cadmium	Cd	112.40	Palladium	Pd	106.7
Caesium	Cs	132.81	Phosphorus	P	31.04
Calcium	Ca	40.07	Platinum	Pt	195.2
Carbon	C	12.005	Potassium	K	39.10
Cerium	Ce	140.25	Praseodymium	Pr	140.9
Chlorin	Cl	35.46	Radium	Ra	226.0
Chromium	Cr	52.0	Rhodium	Rh	102.9
Cobalt	Co	58.97	Ruthenium	Ru	101.7
Columbium	Cb	93.1	Rubidium	Rb	85.45
Copper	Cu	63.57	Samarium	Sa	150.4
Dysprosium	Dy	162.5	Scandium	Sc	44.1
Erbium	Er	167.7	Selenium	Se	79.2
Europium	Eu	152.0	Silicon	Si	28.3
Fluorin	F	19.0	Silver	Ag	107.88
Gladolinium	Gd	157.3	Sodium	Na	23.00
Gallium	Ga	69.9	Strontium	Sr	87.63
Germanium	Ge	72.5	Sulphur	S	32.06
Glucinum	Gl	9.1	Tantalum	Ta	181.5
Gold	Au	197.2	Tellurium	Te	127.5
Helium	He	4.00	Terbium	Tb	159.2
Holmium	Ho	163.5	Thallium	Tl	204.0
Hydrogen	H	1.008	Thorium	Th	232.4
Indium	In	114.8	Thulium	Tm	168.5
Iodin	I	126.92	Tin	Sn	118.7
Iridium	Ir	193.1	Titanium	Ti	48.1
Iron	Fe	55.84	Tungsten	W	184.0
Krypton	Kr	82.92	Uranium	U	238.2
Lanthanum	La	139.0	Vanadium	V	51.0
Lead	Pb	207.20	Xenon	Xe	130.2
Lithium	Li	6.94	Ytterbium (Neoytter-		
Lutecium	Lu	175.0	bium)	Yb	173.5
Magnesium	Mg	24.32	Yttrium	Yt	88.7
Manganese	Mn	54.93	Zinc	Zn	65.37
Mercury	Hg	200.6	Zirconium	Zr	90.6
Molybdenum	Mo	96.0			

CHAPTER XV.

LIGHT.

From a consideration of the applications to which the various pyrotechnic pieces are put, it is evident that the effects to be produced may be divided into two classes:

First, that of illumination only; and, second, where colored effects are desired.

The light which is given off from all sorts of pyrotechnic compositions falls also under two heads:

First, the light which is produced by the incandescence of solids or liquids at a high temperature; and, second, the light which comes from vaporized or gaseous material. Any solid becomes incandescent at a high temperature and the light emitted by it will give a continuous spectrum.

Consider, first, a solid, such as a bar of iron which is in a heated condition. An examination of the spectrum of the light emitted by such a bar will indicate the existence of infra-red radiation before the bar becomes hot enough to be visible. As the temperature is increased the bar becomes incandescent. The spectrum from a bar which is heated just sufficiently to show incandescence will have a preponderance of the light at the red end; as the temperature is increased, so that the appearance of the bar changes from a dull red to a bright red, an examination of the spectrum will show that the bands in the yellow have been intensified. As the temperature is still further increased, the bands beyond the yellow toward the violet end of the spectrum become intensified. It is characteristic of all such incandescent solids that their spectra at any temperature sufficient to produce a spectrum are continuous. They are not characterized by lines, but are without break from one end to the other. This is explained on the theory that the molecules of matter in a solid form are crowded so closely together that they have a very limited radius of movement. On causing these molecules to vibrate

215

rapidly under the influence of heat they interfere with one another, preventing the appearance of individual characteristic activities. This holds both for incandescent solids and for incandescent liquids such as molten iron. In this sort of light emission apparently every possible variation in rapidity of vibration that is represented by the space between the two ends of the spectrum is taking place.

On the other hand, if we consider a luminous vapor, we have an entirely different condition. Here the particles are not sufficiently hampered by their neighbors to undergo interference, but become free to exhibit their individual characteristics. Consequently, in the light from hot vapors the characteristic line spectra of the components appear.

According to this theory it follows that if a gas is caused to emit light when in a state of compression so that the particles crowd each other, and interfere with their free vibration, the lines of its spectrum show some evidences of the continuous-spectrum condition. This is a well-known fact, as tubes of gas under compression when made luminous by the passage of an electric discharge show a very marked widening of their characteristic lines, and it is possible so to compress certain gases that their spectra lose the line characteristic entirely and become continuous.

An interesting example is observed in the spectrum of the atmosphere of the sun. This shows that the characteristic lines of the elements widen as the point observed approaches near and nearer to the actual surface of the sun itself, where the gases exist in a state of compression, owing to the weight of the atmosphere above.

An observation of the solar spectrum shows three different conditions to prevail. In the first place, there is the direct spectrum of the atmosphere of the sun, which has just been mentioned.

In the second place, there is the absorption spectrum which is seen when the light from the sun is viewed through its own atmosphere. This gives the spectrum characterized by the Fraunhofer lines, caused by the absorption by the vapors contained in the sun's atmosphere; and in the third place, a continuous spectrum caused by the incandescence of the sun itself.

As the Fraunhofer lines of the spectrum may be of practical importance in the consideration of colored lights, an explanation of these lines is given briefly as follows:

Light as previously mentioned, which is given off from luminous vapor or gas, is usually composed of waves of a few definite frequencies and no others, corresponding to the definite rates of vibration of the particles comprising the gas. If these light waves of definite frequencies impinge on a quantity of the same gas, the particles of that gas will be set into sympathetic vibratory motion, just as a tuning fork will produce sympathetic vibrations in another fork of the same pitch. If now the gas, which is receiving the radiation, be at a lower temperature than the gas emitting it, the energy of the emitted light will be taken up in these sympathetic vibrations, and if the layer of the cooler gas be thick enough the light may be very largely absorbed. Hence, if the yellow light emitted from incandescent sodium gas impinges upon a sufficient quantity of the same gas, which is not at so high a temperature, it will be almost completely absorbed.

In pyrotechnics an examination of the spectra of the various colored flames shows principally the bright lines characteristic of the various metals used. It becomes of interest, therefore, to examine the effect of temperature and pressure upon these characteristic lines. It has been found in the case of hydrogen at atmospheric pressure, for example, that at certain temperatures its spectrum is characterized by four lines. These lines include one in the red, one in the blue, one in the violet, and one in the extreme violet. As the pressure of the gas is decreased, the continuous spectrum which is emitted at the same time with the characteristic lines decreases and finally vanishes, while the lines themselves become sharper and more distinct. Now, if the pressure is still further reduced, the red and violet lines fade away, leaving the green only. The reverse is true if the pressure is increased.

The appearance of the continuous spectrum accompanying the four-lined spectrum characteristic of hydrogen is caused by the partial interference of the gas particles with one another, which has been mentioned under the discussion of " Incandescent solids," and indicates that as the pressure is reduced, the interference is correspondingly decreased.

Oxygen if excited by a strong spark, produces a number of bright lines, chiefly in the violet, while if a spark of less intensity be used only four lines will remain, which include one in the red, two in the green, and one in the blue. An increase of excitation will introduce new lines, while an increase of pressure will broaden all the lines. With the increase of pressure the number of collisions between the particles is increased and the conditions necessary for the production of a continuous spectrum are realized either in whole or in part. For this reason a gas condensed to approximately its liquid volume will yield a continuous spectrum.

As above indicated an increase in excitation will cause the appearance of additional lines in the spectra of vapors, modifying the color effect. This fact supports the claim of various investigators working with pyrotechnic mixtures, that too high a temperature of combustion seriously affects the strontium reds.

From the above considerations it is clear that in the development of the ideal flare, either for illumination or for the purpose of producing colored light, the temperature must be most carefully worked out in order to attain the desired result.

From this standpoint much study must be given the compositions used as to the temperature produced on combustion. The question becomes a far more complicated one than if the problem of the exact chemical balance between the different substances alone was involved. A mixture of substances so proportioned that the sum total of the chemical actions involved produces the exact consumption of all the components will yield the highest temperature from a theoretical standpoint. A surplus of any one or more of the constituents would consume a part of the heat of combination simply in arriving at the temperature finally attained. This is one source of loss. Another would be that the excess might suffer chemical decomposition requiring heat, as would be the case, for example, if barium nitrate was present in excess above the amount required to combine with the aluminum in the aëroplane flare. In considering the temperature at which the various compositions function the maximum temperature should be ascertained. As pre-

viously discussed this maximum temperature may possibly be too high to give the maximum light efficiency.

It is also evident that the illumination and flame colors may be materially modified by the physical condition in which the compositions are fired. For example, the aëroplane-flare compositions as now compressed might have a different illuminating value if the compression was either increased or decreased, and here again experiment will determine the ideal compression practicable under working conditions. Further, the state of division of the component parts will constitute another modifying factor. When a mixture of hot substances reacts, the more intimately the various substances are mixed the greater will be the efficiency of the mixture so far as the production of a high temperature is concerned. An example of this is the use of both flake and powdered aluminum in certain compositions, the mixtures having been found very advantageous as compared with the use of either alone. As stated, the greater the intimacy of the mixture the greater would be the theoretical efficiency of the composition, but we can not conclude from this that the practical efficiency will be entirely governed by the same rule, as the temperature resulting from the burning of mixtures in which the components are brought into the greatest practical intimacy may be too great to produce the maximum desired effect. These considerations suggest another field for investigation. It is evident, also, that the shape, size, and nature of the containers are bound to have an effect upon the results produced, and the ideal condition can only be ascertained through experiment.

It is well known that many chemical reactions, such as the reduction of carbon dioxide by heated carbon, will not take place unless moisture is present. The amount of the required moisture is extremely small, so small, indeed, that its action may be assumed to be that of a catalyst. At first sight one is tempted to say that the less moisture a composition contains the greater will be its efficiency, but here again it will be safer to leave the final conclusion to experiment rather than to accept the statement without proof.

Pyrotechnic pieces that are stored over considerable periods of time may be subject to the changes and deteriorations discussed in the chapter on storage. It may be,

however, that the changes produced during storage have effects that are to be desired. Probably these effects will be small, but they should at least be investigated.

Summarizing the various factors, both physical and chemical, which may affect the result desired from a pyrotechnic piece intended for illumination only, we should note the following:

First. The purity of each substance used.

Second. The chemical balance of the composition as a whole.

Third. The amount of moisture present.

Fourth. The age of the composition, taking into account the slow chemical reactions which may take place with the lapse of time.

Fifth. The relation of the proportions of the various substances used, as compared with the ideal relation experimentally determined as producing the greatest efficiency.

Sixth. The relative fineness of the various constituents.

Seventh. The degree of compression used in the formation of the composition.

Eighth. The thoroughness with which the various constituents have been mixed.

Ninth. The shape and size of the finished piece in which the composition functions.

Tenth. The hygroscopic properties of the composition as a whole.

Eleventh. The efficiency and adaptability of the container as regards the maximum effect to be produced.

When we come to a consideration of the compositions for producing colored-flame effects, the same general considerations regarding their physical condition must be taken into account, as in the case of the mixtures designed to produce an illumination only. In addition to these considerations, however, more attention must be paid to determining the temperatures at which the colored effects will be at a maximum. This has been explained in the discussion on light. There must be some temperature at which the strontium red is at a maximum, for example, and these temperatures of maximum depth of color effect should be carefully studied. Further, their study will show that these maximum color temperatures are modified by the physical condition of the mixtures, such as fineness, degree of compression, nature

of the container, and all of the items mentioned under the illumination effect.

Under these general considerations we have attempted to give an outline of the nature of the investigations which should be undertaken in the future, in order to perfect the art of military pyrotechnics from the physical and chemical standpoint.

During the progress of the work, the results of which are recorded in this book, and from the many conferences and discussions held for the purpose of considering the various problems, many detached questions presented themselves, which should receive future consideration. They may be summarized as follows:

First. The development of a method for determining the shade and candle-power of a colored flame simultaneously.

Second. A study of the visibility of colored flames at various distances. For example, it has been indicated that a barium flame may cease to appear green at a distance.

Third. A study of the penetrating power of colored flames through such media as clouds of mist, smoke, dust, etc.

Fourth. The development of a green flame without using barium salts. Many references are made in the literature to the use of certain salts of copper for this purpose, but the work up to date was not successful with these compounds.

Fifth. The consolidation and revision of specifications for the various pyrotechnic pieces, including the establishment of color and candlepower requirements, the volume of smoke formed on functioning, and the stability on aging.

Sixth. The investigation of potassium-perchlorate mixtures, having in mind the greater safety of compositions including this compound as compared with those in which potassium chlorate is used.

Seventh. The development of a set of standard colored signals, all of which should have the same visibility.

Eighth. The limiting of colored signals to red and green, with the addition of amber (sodium yellow), and the use of white light only for illumination.

Ninth. The development of a substitute for shellac which can be produced in this country.

Tenth. The study of a method for overcoming the chimneying effect, now common to pyrotechnic pieces in paper or

cardboard containers. This has special reference to the use of metallic containers.

Eleventh. The development of a "stickless" rocket.

Twelfth. The substitution of barium nitrate for potassium nitrate in the propelling charge of rockets.

Doubtless very many other problems will present themselves as these investigations progress. It is impossible to foretell what they will be, but they should be investigated as they appear.

INDEX.

O